JOURNAL

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ABSTRACTS OF PAPERS

ON

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1903.

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REPORT OF

THE INTERNATIONAL COMMITTEE

ON ATOMIC WEIGHTS.

The International Committee on Atomic Weights * has the honour to offer the following report:

In the table of atomic weights for 1904, only two changes from 1903 are recommended. The atomic weight of cæsium has been slightly modified to accord with the recent determinations by Richards and Archibald, and that of cerium in conformity with the measurements by Brauner. The value for lanthanum is still in controversy, and any change here would therefore be premature. The same consideration may also be urged with regard to iodine. Ladenburg has shown that the accepted number for iodine is probably too low, but other investigations upon the subject are known to be in progress, and until they have been completed it would be unwise to propose any alteration.

Many of the atomic weights given in the table are well known to be more or less uncertain. This is especially true with respect to the rarer elements, such as gallium, indium, columbium, tantalum, &c. But some of the commoner elements also stand in need of revision, and we venture to call attention to a few of these. Among the metals, the atomic weights of mercury, tin, bismuth, and antimony should be redetermined, for the reason that the existing data are not sufficiently concordant. Palladium also, on account of discrepancies between different observers, and possibly vanadium, for which the data are too few, deserve some attention. Among the non-metals, phosphorus has been peculiarly neglected, and our knowledge of the atomic weight of silicon rests upon a single ratio. In the latter case, confirmatory data are much to be desired. Upon any of these elements, new investigations would be most serviceable.

There is one other point to which we may properly call attention. Many of the ratios from which atomic weights have been calculated were measured in vessels of glass, by processes involving the use of

* The original members of the Committee take great pleasure in announcing the addition to their number of Professor Henri Moissan. They are confident that this increase will meet with universal approval.

strong acids. In such cases, the solubility of the glass becomes an important consideration, even when no transfer of material from one vessel to another has occurred. A slight conversion of silicate into chloride would cause an increase of weight during the operation, and so introduce an error into the determination. Such errors are doubtless very small, but still they ought not to be neglected. Now that vessels of pure silica, the so-called quartz-glass, are available for use, they might well replace ordinary glass in all processes for the determination of atomic weights. An investigation into the relative availability of the two kinds of glass is most desirable.

F. W. Clarke
T. E. Thorpe
K. Seubert
Henri Moissan
} *Committee.*

1904.

INTERNATIONAL ATOMIC WEIGHTS.

		O=16.	H=1.
Aluminium	Al	27·1	26·9
Antimony	Sb	120·2	119·3
Argon	A	39·9	39·6
Arsenic	As	75·0	74·4
Barium	Ba	137·4	136·4
Bismuth	Bi	208·5	206·9
Boron	B	11	10·9
Bromine	Br	79·96	79·36
Cadmium	Cd	112·4	111·6
Cæsium	Cs	132·9	131·9
Calcium	Ca	40·1	39·8
Carbon	C	12·00	11·91
Cerium	Ce	140·25	139·2
Chlorine	Cl	35·45	35·18
Chromium	Cr	52·1	51·7
Cobalt	Co	59·0	58·56
Columbium (Niobium)	Cb	94	93·3
Copper	Cu	63·6	63·1
Erbium	Er	166	164·8
Fluorine	F	19	18·9
Gadolinium	Gd	156	155
Gallium	Ga	70	69·5
Germanium	Ge	72·5	71·9
Glucinum (Beryllium)	Gl	9·1	9·03
Gold	Au	197·2	195·7
Helium	He	4	4
Hydrogen	H	1·008	1·000
Indium	In	114	113·1
Iodine	I	126·85	125·90
Iridium	Ir	193·0	191·5
Iron	Fe	55·9	55·5

		O=16.	H=1.
Krypton	Kr	81·8	81·2
Lanthanum	La	138·9	137·9
Lead	Pb	206·9	205·35
Lithium	Li	7·03	6·98
Magnesium	Mg	24·36	24·18
Manganese	Mn	55·0	54·6
Mercury	Hg	200·0	198·5
Molybdenum	Mo	96·0	95·3
Neodymium	Nd	143·6	142·5
Neon	Ne	20	19·9
Nickel	Ni	58·7	58·3
Nitrogen	N	14·04	13·93
Osmium	Os	191	189·6
Oxygen	O	16·00	15·88
Palladium	Pd	106·5	105·7
Phosphorus	P	31·0	30·77
Platinum	Pt	194·8	193·3
Potassium	K	39·15	38·86
Praseodymium	Pr	140·5	139·4
Radium	Ra	225	223·3
Rhodium	Rh	103·0	102·2
Rubidium	Rb	85·4	84·8
Ruthenium	Ru	101·7	100·9
Samarium	Sm	150	148·9
Scandium	Sc	44·1	43·8
Selenium	Se	79·2	78·6
Silicon	Si	28·4	28·2
Silver	Ag	107·93	107·12
Sodium	Na	23·05	22·88
Strontium	Sr	87·6	86·94
Sulphur	S	32·06	31·83
Tantalum	Ta	183	181·6
Tellurium	Te	127·6	126·6
Terbium	Tb	160	158·8
Thallium	Tl	204·1	202·6
Thorium	Th	232·5	230·8
Thulium	Tm	171	169·7
Tin	Sn	119·0	118·1
Titanium	Ti	48·1	47·7
Tungsten	W	184·0	182·6
Uranium	U	238·5	236·7
Vanadium	V	51·2	50·8
Xenon	X	128	127
Ytterbium	Yb	173·0	171·7
Yttrium	Yt	89·0	88·3
Zinc	Zn	65·4	64·9
Zirconium	Zr	90·6	89·9

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.

2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.

6. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.

7. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

8. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

9. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

10. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

11. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ*.

12. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

13. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ α-cyanopropane.

14. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,

$$\begin{matrix}CH_3\\ CH_3\cdot CH_2\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\ CH_3\end{matrix} \quad \text{or} \quad CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$$

should be termed $\beta\gamma$-dimethylpentane, not methylethyl*iso*propylmethane, and $\begin{matrix}CH_3\\ CH_3\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\ CO_2H\end{matrix}$ or $CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$ should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

15. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

16. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

17. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

18. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt{\cdot}CHMe{\cdot}CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3{\cdot}CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc{\cdot}CHMe{\cdot}CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6HEt_2(OH)_2{\cdot}CO_2H$, and not $C_6H_3(OEt)_2{\cdot}CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}CO_2H$.

19. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

20. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, β-anilino-acrylic acid, $NHPh{\cdot}CH{:}CH{\cdot}CO_2H$, α-iminopropionic acid, $NH{:}CMe{\cdot}CO_2H$.

21. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

22. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

23. The Collective Index, 2nd decade (1883—1892) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

24. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

25. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

26. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

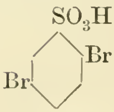
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

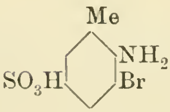
27. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

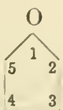
(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

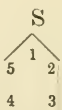
(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed ; for example :—

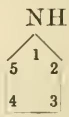

is 2 : 5-dibromobenzenesulphonic acid ;

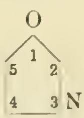

is 3-bromo-*o*-toluidine-5-sulphonic acid.

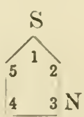
28. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (2nd edition, 1899, pp. 16—26) should be used, of which the following schemes may be regarded as typical :—

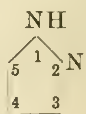

Furan.

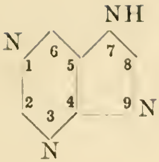

Thiophen.


Pyrrole.


Oxazole.

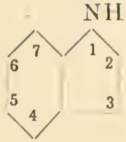

Thiazole.


Pyrazole.



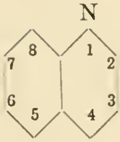
Purine.*

Pyridine.

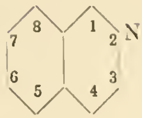


Indole.

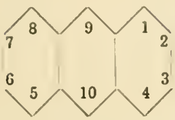
Naphthalene.



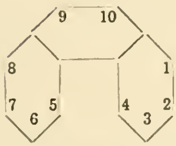
Quinoline.



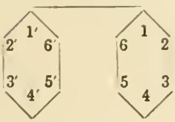
*iso*Quinoline.



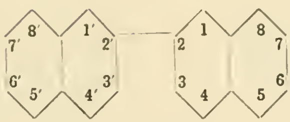
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

29. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

30. Not more than one abstract must appear on a sheet.

31. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

32. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

33. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

34. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

***** The Editor's decision, in all matters connected with the Abstracts, must be considered final.**

* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

Abbreviated Title.	Journal.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Agron.	Annales agronomiques.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path.	Beiträge für chemische Physiologie und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
* *Bied. Centr.*	Biedermann's Centralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bihang K. Svenska Vet.-Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Soc. chim.	Bulletin de la Société chimique de Paris.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Centr.*	Chemisches Centralblatt.
Chem. News	Chemical News.

* Abstracts from the *Centralblatt* are made only in the case of papers published in journals other than those included in this list.

ABBREVIATED TITLE.	JOURNAL.
Chem. Rev. Fett- Harz- Ind.	Chemische Revue uber die Fett- und Harz Industrie.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Fed. Inst. Brewing.	Journal of the Federated Institutes of Brewing.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal fur praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Milch Zeit.	Milch Zeitung.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Ofver K. Vet.-Akad. Forh.	Ofversigt af Kongl. Vetenskaps-Akademiens Forhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch.	Pharmaceutical Archives.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Roy. Soc.	Proceedings of the Royal Society.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada.	Transactions of the Royal Society of Canada.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitth.	Tschermak's Mineralogische Mittheilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Farb. Text. Chem.	Zeitschrift für Farben- und Textil-Chemie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeit. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeit. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeit. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeit. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Elementary Composition of Russian Naphthas and the Basis for Classifying them. K. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 629—632).—The author finds that as a basis for classifying Russian naphthas of different origins the elementary composition is of little value. A number of analyses of such naphthas have been made, the results of which indicate that the factors of use for classification are the percentages of paraffins, tar, sulphur, nitrogen, and heavy lubricating oil. T. H. P.

Conversion of Trimethylene into Propylene. SIMEON TANATAR (*Zeit. physikal. Chem.*, 1902, 41. 735—738. Compare Tanatar, Abstr., 1896, i, 457; Berthelot, Abstr., 1899, i, 872).—It is shown that the conversion of trimethylene into propylene takes place at 100° under the catalytic influence of platinum black, the quantity converted in 120 hours amounting to 40 per cent. Light, on the other hand, has neither an accelerating nor a retarding effect.

The author explains his views on isomerism as interpreted in terms of the energy of rotation of the atoms. J. C. P.

Ethylene and Ethylidene Dichlorides. HEINRICH BILTZ (*Ber.*, 1902, 35, 3524—3528).—Ethylene and ethylidene dichlorides are both decomposed at a red heat into an equal number of molecules of chloroethylene and hydrogen chloride.

Chloroethylene combines with bromine, forming α-chloro-αβ-dibromoethane, and with chlorine, forming *ααβ-trichloroethane*, which boils at 113·5—114·5° under 756 mm. pressure and is readily acted on by

chlorine. α-Chloro-αβ-dibromoethane is readily converted by the action of alcoholic ammonia into α-chloro-β-bromoethylene, which boils at 61—62° under 772 mm. pressure. R. H. P.

Propylene Monochlorohydrins. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1902, 535—536).—Propylene α-monochlorohydrin boils at 133—134° and propylene β-monochlorohydrin at 126—127° under 760 mm. pressure. A similar difference in the boiling point is found in the case of the isomeric dichlorohydrins, $CH_2Cl\cdot CHCl\cdot CH_2\cdot OH$ (b. p. 182°) and $CH_2Cl\cdot CH(OH)\cdot CH_2Cl$ (b. p. 176—177°). A. F.

Saponification of Nitro-ethers. LÉO VIGNON and I. BAY (*Compt. rend.*, 1902, **135**, 507—509).—The nitrates derived from methyl alcohol, ethyl alcohol, glycerol, erythritol, pentaerythritol, mannitol, and dulcitol are not saponified by heating with water on the water-bath; when heated with water in sealed tubes at 110—120°, complete solution takes place and nitric and nitrous acids are formed, nitrogen being at the same time liberated. The saponification with sulphuric acid and with sodium hydroxide is slow. In the case of the action of alkali, it was observed that a small amount of sodium dioxide was produced. J. McC.

Decompositions of Bistrimethylethylene Nitrosate. JULIUS SCHMIDT and PATRIC C. AUSTIN (*Ber.*, 1902, **35**, 3721—3727. Compare Abstr., 1902, i, 582).—Sodium methoxide converts bis-trimethylethylene nitrosate into methylmethoxy*iso*propylketoxime. The reaction probably consists first in the transformation of the bis-compound into the unimolecular compound, $NO_2\cdot O\cdot CMe_2\cdot CHMe\cdot NO$, this is then converted into the isomeride, $NO_2\cdot O\cdot CMe_2\cdot CMe:NOH$, which reacts with the methoxide, yielding *methylmethoxy*iso*propylketoxime*, $OMe\cdot CMe_2\cdot CMe:N\cdot OH$. This crystallises from light petroleum in colourless prisms melting at 92—93° and distils at 190° under 742 mm. pressure, possesses a characteristic odour, is volatile with steam, and is readily soluble in most solvents including acids and alkalis. When hydrolysed with concentrated hydrochloric acid, it yields the theoretical amount of hydroxylamine together with *methyl hydroxy*iso*propyl ketone* in the form of a colourless liquid distilling at 141—142° under 745 mm. pressure and yielding a *semicarbazone*, $OH\cdot CMe_2\cdot CMe:N\cdot NH\cdot CO\cdot NH_2$, melting at 164—165°. The *benzoyl* derivative of the ketoxime melts at 74—75°.

Attempts to obtain ethoxy- and propyloxy-derivatives by the action of sodium ethoxide and propyloxide on bistrimethylethylene nitrosate gave negative results.

Methylcyano*iso*propylketoxime, $CN\cdot CMe_2\cdot CMe:N\cdot OH$ (Wallach, Abstr., 1889, 233) has the simple molecular formula and yields a *benzoyl* derivative melting at 64°. J. J. S.

Polymerism and Desmotropism of Trimethylethylene Nitrosochloride (γ-Chloro-β-nitroso-β-methylbutane). JULIUS SCHMIDT [and, in part, with PATRIC C. AUSTIN] (*Ber.*, 1902, **35**, 3727—3737. Compare Abstr., 1902, i, 581 and 582).—The amylene nitrosochloride

of Tönnies (*Ber.*, 1879, **12**, 169, and Tilden and Sudborough, Trans., 1893, **63**, 483), melting at 74—75°, is shown by cryoscopic determinations in ethylene bromide and benzene to be bimolecular and is called bistrimethylethylene nitrosochloride. It gives Liebermann's nitroso-reaction and when heated for a short time at 75°, or when warmed with ether, is converted into the unimolecular compound *γ-chloro-β-nitroso-β-methylbutane* (trimethylethylene nitrosochloride). It is a bluish-green liquid which, on cooling, readily polymerises; it liberates iodine from potassium iodide solution, and on reduction yields ammonia. When boiled with concentrated nitric acid, it yields *βγγ-trinitro-β-methylbutane*, $NO_2 \cdot CMe_2 \cdot CMe(NO_2)_2$ (?), in the form of small prisms decomposing at about 203°, and readily soluble in most solvents. *Methylchloroisopropylketoxime*, $CMe_2Cl \cdot CMe \colon N \cdot OH$, is formed by the transformation of the nitrosochloride when the bimolecular compound is heated at 75° and rapidly stirred until the colour is pale yellow. It crystallises in colourless plates softening at 45° and melting at 49—50°; at 90° it partially resolidifies, and decomposes at 130°. It is volatile at the ordinary temperature, has a strong odour, and does not give Liebermann's reaction. On treatment with sodium methoxide, it yields methylmethoxy*iso*propylketoxime (compare preceding abstract). Its *benzoyl* derivative, $CMe_2Cl \cdot CMe \colon N \cdot OBz$, crystallises from alcohol in colourless needles melting at 53—54° and its *phenylcarbimide* derivative forms glistening prisms melting at 109°. On hydrolysis with hydrochloric acid, the ketoxime yields methyl hydroxy*iso*propyl ketone and hydroxylamine hydrochloride. J. J. S.

Trimethylethylene Nitrosite. A Reply to Hantzsch. Julius Schmidt (*Ber.*, 1902, **35**, 3737—3740. Compare Hantzsch, Abstr., 1902, i, 734).—Polemical. J. J. S.

General Method of Synthesising Monohydric Alcohols. Marcel Guerbet (*Ann. Chim. Phys.*, 1902, [vii], **27**, 67—105).—A detailed account of work already published (compare Abstr., 1899, i, 471, 472; 1901, i, 182, 307, 625; 1902, i, 130, 335, 583, 657).

Tetraheptyl alcohol,

$$CH_3 \cdot [CH_2]_6 \cdot CH(C_4H_9) \cdot CH_2 \cdot CH_2 \cdot C(C_4H_9)(C_7H_{15}) \cdot CH_2 \cdot CH_2 \cdot OH,$$

produced by heating 2 mols. of diheptyl alcohol with 1 atomic proportion of sodium at 230—250°, is a colourless, odourless liquid boiling at 295—300° under 13 mm. pressure and having the sp. gr. 0·8514 at 0° and 0·8418 at 15°. G. T. M.

Calculation of the Number of Classes of Saturated Polyhydric Alcohols and their Oxidation Products. Richard Anschütz (*Ber.*, 1902, **35**, 3457—3463).—The general formula,

$$\frac{m(m+1)(m+2)\;.\;.\;.\;.\;(m+n-1)}{1\;.\;2\;.\;3\;.\;.\;.\;.\;.\;.\;.\;.\;n},$$

gives the number of classes of compounds containing a certain radicle combined n times in m different ways.

All alcohols contain one or more of one, two, or three of the radicles $CH_2 \cdot OH$, $CH \cdot OH$, and $C \cdot OH$, so that in this case $m = 3$ and the calcu-

lated number of classes of n-hydric alcohols are 3, 6, 10, 15, 21, and 28 when n is 1, 2, 3, 4, 5, and 6 respectively.

The oxidation products of the alcohols having no hydroxyl groups contain their oxygen atoms in one or more of the following radicles, ·CHO, :CO, and ·CO_2H. In this case also $m = 3$, so that the number of classes of non-hydroxylic oxidation products is equal to the number of the series of the corresponding alcohols.

The oxidation products containing hydroxyl may contain the groups ·CH_2·OH, :CH·OH, ⋮C·OH, ·CHO, :CO, ·CO_2H or $m = 6$, and hence the numbers of different series of these substances produced from the n-hydric alcohols are 0, 9, 36, 96, 210, and 406 when n is 1, 2, 3, 4, 5, and 6 respectively. The communication contains these and other results exhibited in tabular form together with suggestions as to the nomenclature of compounds of mixed alcoholic, aldehydic, ketonic, and carboxylic functions. G. T. M.

New Synthesis of Sorbic Acid and its Homologues. W. Jaworsky and Sergius N. Reformatzky (*Ber.*, 1902, **35**, 3633—3639).—The ethyl esters of β-hydroxysorbic acid and its homologues may be generally obtained by condensing crotonaldehyde in the presence of zinc with the α-bromo-derivatives of ethyl acetate, propionate, butyrate, and *iso*butyrate; intermediate organic zinc bromides are produced which are readily decomposed by wet ether, giving rise to the corresponding esters, CHMe:CH·CH(OH)·CRR^1·CO_2Et, and from these substances the acids are readily obtained by hydrolysis.

Acids of the sorbic series are produced by the elimination of water from the molecules of these hydroxy-acids, and in this class of compounds the hydrogen which unites with the hydroxyl group is taken from the α-position. The elimination of water is effected in some cases simply by boiling the hydroxy-compound with 20 per cent. barium hydroxide solution; β-hydroxy-α-methyl- and α-ethyl-hydrosorbic acids, on the other hand, require a solution of sodium hydroxide at 150°.

The *ethyl* esters of *β-hydroxyhydrosorbic*, *β-hydroxy-α-methylhydrosorbic*, *β-hydroxy-α-ethylhydrosorbic*, and *β-hydroxy-αα-dimethylhydrosorbic* acids are mobile liquids with a fruity odour, insoluble in water but dissolving in ether or alcohol; they boil at 100° (2 mm. pressure), 110—112° (15 mm.), 128—130° (15 mm.), and 118—120° (17 mm.) respectively. The corresponding acids are oily liquids insoluble in water but readily soluble in alcohol, ether, or benzene; their *silver* salts are soluble in water.

Potassium β-hydroxy-α-methylhydrosorbate and hydroxy-αα-dimethyl-β-hydrosorbate are soluble salts crystallising respectively with $1\frac{1}{2}$ and 1 mol. of water; the *sodium* salt of the latter acid contains $5H_2O$.

α-Methylsorbic and *α-ethylsorbic acids*, when freshly prepared, melt at 90—92° and 75—77° respectively, the melting point, however, gradually falls until the substances pass into a thick yellow oil.

G. T. M.

Camphocarboxylic Acid. I and II. Julius W. Brühl (*Ber.*, 1902, **35**, 3510—3519; 3619—3633).—Camphocarboxylic acid is purified

from borneol by repeated crystallisation from benzene; it crystallises from ether or 50 per cent. alcohol in well defined prisms.

iso*Amyl camphocarboxylate* is a colourless, odourless oil boiling at 175—175·5°.

The acid itself develops only a transient coloration with ferric chloride; the colour reaction is, however, more pronounced in the case of the alkyl esters. Small quantities of these derivatives develop a green coloration with alcoholic ferric chloride which changes successively to red and yellow on adding sodium acetate. An indigo blue coloration is developed in more concentrated solutions which gradually changes to green, and becomes red on the addition of sodium acetate.

The methyl ester dissolves in semi-normal sodium hydroxide solution containing the calculated amount of the alkali, and is reprecipitated unchanged by the action of acid; it is extracted from very dilute alkaline solutions by shaking with ether. The ethyl ester is almost insoluble in dilute solutions of sodium hydroxide, dissolving, however, when the solution is more concentrated. The amyl ester is quite insoluble in concentrated solutions of sodium hydroxide. The three esters give a distinctly acid reaction with blue litmus paper.

Although these esters behave so differently towards sodium hydroxide, yet a study of their optical properties shows that they all have the ketonic structure $C_8H_{14}<\begin{matrix}CH\cdot CO_2R\\ |\\ CO\end{matrix}$. The specific dispersion of the three compounds varies only through very narrow limits, the extreme values of $M_\gamma - M_\alpha$ being 0·0064 and 0·0067.

The physical properties of the esters (boiling point, sp. gr. refractive indices for Na, H_α, H_β, and H_γ, and the molecular refractions and dispersions) are tabulated. Kachler and Spitzer (Abstr., 1882, 66) found that camphocarboxylic acid in ethereal solution interacted with metallic sodium to form the compound $C_{21}H_{31}O_6Na$; this substance is also produced in benzene solution, and separates, on warming, as a gelatinous precipitate; it is not converted into a methyl ester by the action of methyl iodide.

Sodium camphocarboxylate has no action on the nervous and circulatory systems of cold- and warm-blooded animals, and is found unchanged in the urine. The ethyl ester, when subcutaneously or intravenously administered, behaves like camphor and produces convulsions and paralysis, the methyl ester has a less marked physiological action; the amyl ester produces no immediate effect, but, after 24 hours, convulsions set in, followed by death.

The alkyl esters of the substituted camphocarboxylates having the general formula $C_8H_{14}<\begin{matrix}CR\cdot CO_2R'\\ |\\ CO\end{matrix}$ are hydrolysed only with great difficulty by aqueous or alcoholic alkali hydroxides at high temperatures, and are not affected by mineral acids. In this respect, these esters differ altogether from their lower homologues, having hydrogen in the place of the radicle R, since the latter undergo hydrolysis with great readiness.

The substituted esters may, however, be hydrolysed by concentrated solutions of the alkali alkyloxides in the corresponding alcohols, this

reaction taking place even in the cold, and being greatly accelerated by gentle heating.

Methylcamphocarboxylic acid, $C_8H_{14}<\begin{matrix}CMe\cdot CO_2H \\ | \\ CO\end{matrix}$, prepared in this way from its methyl ester, crystallises in well-defined prisms melting at 104° and decomposing into methylcamphor and carbon dioxide; it is readily soluble in the ordinary organic solvents and in warm water. An oily compound is also formed in this hydrolysis which is possibly a stereoisomeride of the preceding acid.

The sodium derivatives of the alkyl camphocarboxylates do not react with alkyl iodides in non-dissociating media such as ether or benzene. In the presence of dissociating liquids (alcohols), they react like other sodio-β-ketonic esters. It is supposed that the enolic form $C_8H_{14}<\begin{matrix}C\cdot CO_2R \\ \| \\ C\cdot ONa\end{matrix}$, exists in the former media, whilst the ketonic modification, $C_8H_{14}<\begin{matrix}CNa\cdot CO_2R \\ | \\ CO\end{matrix}$, is formed in alcoholic solution. Since the product is of the ketonic form, it is assumed that only the latter sodium derivative reacts with the alkyl iodide.

Methyl allylcamphocarboxylate, $C_8H_{14}<\begin{matrix}C(C_3H_5)\cdot CO_2Me \\ | \\ CO\end{matrix}$, produced by adding a 12 per cent. solution of sodium in methyl alcohol to a mixture of methyl camphocarboxylate and allyl iodide, separates from aqueous alcohol in colourless crystals melting at 75·5—76°. The crystalline product is accompanied by a colourless oil boiling at 159·5—161° under 13 mm. pressure; this substance is either a stereoisomeride or the same compound contaminated with a trace of impurity. When hydrolysed with sodium methoxide at 150°, the preceding ester gives rise to *allylhomocamphoric acid*, $CO_2H\cdot C_8H_{14}\cdot CH(C_3H_5)\cdot CO_2H$; this product crystallises from dilute alcohol in needles melting at 163°, and is a dibasic acid forming the *silver* salt, $C_{14}H_{20}O_4Ag_2$.

Ethyl allylcamphocarboxylate, prepared from ethyl camphocarboxylate, sodium ethoxide, and an 8 per cent. solution of sodium in methyl alcohol, is an odourless, colourless oil boiling at 163—164° under 12·5 mm. pressure, which, when hydrolysed with an alcoholic sodium ethoxide solution on the water-bath, yields allylhomocamphoric acid.

Lists are given of the physical constants of the preceding compounds.

G. T. M.

Compounds of Mesoxalic Acid and Glyoxylic Acid with Guanidine. L. Kaess and J. Gruszkiewicz (*Ber.*, 1902, **35**, 3600—3607).—To prepare mesoxalic acid, the authors recommend decomposing barium alloxanate with nitrous acid. In alcoholic solution, ethyl mesoxalate combines with guanidine, giving *ethyl guanidine mesoxalate*, $NH{:}C(NH_2)\cdot NH\cdot CO\cdot C(OH)_2\cdot CO_2Et$, which crystallises from water in small, colourless prisms, loses $1H_2O$ at 105°, and becomes yellow without melting at 195°. *Mesoxalylguanidine*, $C(OH)_2<\begin{matrix}CO\cdot NH \\ CO\cdot NH\end{matrix}>C{:}NH$, obtained by adding an ammoniacal solution

of silver oxide to dibromomalonylguanidine, is a colourless substance which, when heated, decomposes without melting. Attempts to condense ethyl mesoxalate with *s*-dimethylguanidine did not give a definite compound.

Glyoxylic acid does not yield glyoxylguanidine with guanidine; on warming the base with the acid (1 mol.) in alcoholic solution, a *substance*, $C_{12}H_{32}O_{25}N_{12}$, is obtained which crystallises from alcohol in well-formed, transparent, rhombic prisms, and melts at 167°. The residue undissolved by alcohol contains a *substance*, $C_{15}H_{24}O_{19}N_{12}$, which melts at 207°, and is extracted by ammonia, precipitated from the solution by acid, and crystallised from water; the portion insoluble in ammonia, on recrystallisation from water, gives slender needles of the compound $C_4H_7O_2N_5$ (Doebner and Gaertner, Abstr., 1901, i, 261), which is probably a *glyoxylbiguanide*, $\begin{matrix}CH(OH)\cdot NH\cdot C(:NH) \\ | \\ CO\text{———}NH\cdot C(:NH)\end{matrix}\!\!>\!NH$. If the action between guanidine and glyoxylic acid takes place at the ordinary temperature in alcoholic solution, the *substance* $C_{15}H_{21}O_{19}N_2$ is the principal product, but two other crystalline *substances*, $C_{11}H_{21}O_{16}N_9$ and $C_6H_{16}O_{14}N_6$, are formed which melt and decompose at 125° and 160° respectively.

In alcoholic solution, at the ordinary temperature, guanidine carbonate and glyoxylic acid give a *substance*, $C_9H_{23}O_{10}N_9$, which crystallises from water in small needles and melts at 187° (contrast Doebner and Gaertner, *loc. cit.*). W. A. D.

Standard Tartar Emetic Solution and the Structural Formula of the Salt. F. E. HALE (*J. Amer. Chem. Soc.*, 1902, 24, 828—847).—When a standard solution of tartar emetic is made up, a discrepancy is usually observed between its titre and that of an arsenite solution with respect to a standard iodine solution. This is due to the fact that the amount of water in solid tartar emetic is not constant. The salt shows a great tendency to lose its water of crystallisation; in the form of fine crystals or powder, it loses water slowly in the air, more rapidly over sulphuric acid, and even in closed bottles a little is lost. At 128—130°, the dried salt loses nearly $\frac{1}{2}H_2O$, and at 165° it parts with $1H_2O$. The formation of these anhydrides leads the author to assume that the antimony replaces the hydrogen of the alcoholic hydroxyl of the tartaric acid and not that of the carboxyl group. A standard solution of tartar emetic is best prepared from a salt which has been separated in medium-sized (1/32 to $\frac{1}{4}$ inch) crystals which have been dried first by suction and then by exposure for three to four hours in the air at a temperature not exceeding 25°. J. McC.

Conversion of *d*-Glycuronic Acid into *l*-Xylose. ERNST SALKOWSKI and CARL NEUBERG (*Zeit. physiol. Chem.*, 1902, 36, 261—267).—A number of cases are known in which ferments, organised or unorganised, produce the elimination of carbon dioxide from an organic acid.

It is now shown that *d*-glycuronic acid is transformed into *l*-xylose by the elimination of carbon dioxide when a mixture of ordinary

bacteria of putrefying meat is grown in a slightly alkaline solution of the acid. The unaltered acid may be separated from the *l*-xylose by precipitation as a basic lead salt. The reaction confirms Fischer and Piloty's constitution for glycuronic acid (Abstr., 1891, 677).

J. J. S.

Formation of Formaldehyde from Methyl Alcohol under the Influence of Colloidal Metallic Solutions. Arthur Glaessner (*Chem. Centr.*, 1902, ii, 731—732; from *Oesterr. Chem.-Zeit.*, 5, 337—338).—When air is passed through methyl alcohol in presence of Bredig's solution of colloidal platinum (Abstr., 1900, ii, 213), a small quantity of formaldehyde is formed. A solution of colloidal copper was found to be less effective. E. W. W.

Formation of Aldehydes and Ketones from α-Glycols and from α-Oxides. K. Krassusky (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 537—555).—It has been shown by the author (Abstr., 1902, i, 261 and 425) that in the formation of aldehydes and ketones from β-chloro-alcohols or from haloid derivatives of ethylene hydrocarbons, organic oxides or glycols are obtained as intermediate products of the reactions. Further investigations have now been made, the results of which demonstrate that glycols represent the first stage of this change, the oxides only appearing as intermediate steps in the transformation of the glycols into aldehydes or ketones.

Experiments with ethylene glycol, propylene glycol, ψ- and *iso*-butylene glycols, and trimethylethylene glycol show that, in the absence of an acid, the α-glycols do not decompose into water and aldehyde or ketone, even at high temperatures. Small quantities of acid, however, bring about this decomposition, which may be represented by the following equations:

(1) $mC_nH_{2n}(OH)_2 + C_nH_{2n}(OH)Cl = mC_nH_{2n}(OH)_2 + C_nH_{2n}O + HCl$

(2) $mC_nH_{2n}(OH)_2 + HCl = (m-1)C_nH_{2n}(OH)_2 + C_nH_{2n}(OH)Cl + H_2O.$

Experiments on the action of zinc chloride on ethylene oxide, propylene oxide, ψ- and *iso*-butylene oxides, trimethylethylene oxide, hexylene oxide, and tetramethylethylene oxide show that these compounds are converted into aldehydes or ketones more readily than the corresponding glycols. Further, trimethylethylene oxide is converted into methyl *iso*propyl ketone and ψ- and *iso*-butylene oxides yield aldehydes when heated with lead chloride at temperatures at which the corresponding glycols remain almost entirely unchanged.

The author applies the results obtained by him to explain the observations of various other investigators. T. H. P.

Mechanism of the Isomerisation of α-Oxides. K. Krassusky (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 556—575. Compare preceding abstract).—The author first gives the views of various authors with regard to the mechanism of the transformation of organic α-oxides into aldehydes or ketones, and from a consideration of their results and his (*loc. cit.*) develops his own views, which are as follows: (1) The combination of hypochlorous acid with olefines

mainly proceeds in such a way that the hydroxyl group becomes attached to the carbon atom combined with the smallest number of hydrogen atoms. (2) The same is the case for the combination of the organic α-oxides with hypochlorous acid. (3) The analogy drawn by Würtz between the behaviour of the organic α oxides and the oxides of bivalent metals must hence be regarded as a limited one. (4) Typical organic α oxides cannot be formed in acid media. (5) In alkaline or neutral media, α-chloro-alcohols are resolved into α-oxides and hypochlorous acid; in acid media, into aldehydes or ketones and hypochlorous acid; and under the influence of dehydrating agents into chloroethylenes and water. (6) The formation of glycols from haloid compounds of olefines or from α-haloid-alcohols under the action of water in presence of lead oxide proceeds through the organic α-oxides. (7) The readiness of α-haloid-alcohols to form aldehydes and ketones is related to their readiness to undergo dissociation. (8) The conversion of organic α-oxides into aldehydes and ketones under the influence of zinc chloride or lead chloride may be used as a means of determining the structure of the α-oxides. For zinc chloride, the reaction is exemplified by the following equation:

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O + ZnCl_2 = \begin{array}{l}CH_2\cdot OCl\\ |\\ CH_2\cdot ZnCl\end{array} = \begin{array}{l}CH{:}O\\ |\\ CH_2\cdot ZnCl\end{array} + HCl = \begin{array}{l}CH{:}O\\ |\\ CH_3\end{array} + ZnCl_2.$$

T. H. P.

Preparation of *r*- and *l*-Galactose. CARL NEUBERG and JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1902, 36, 219—226. Compare Fischer and Hertz, Abstr., 1892, 826).—*r*-Galactose is most readily obtained by the oxidation of dulcitol with a 3 per cent. solution of hydrogen peroxide in the presence of barium carbonate and ferrous sulphate. The solution is evaporated and mixed with 95 per cent. alcohol, when the inorganic salts are precipitated. The sugar itself may be obtained directly from the alcoholic liquid, but a better yield is obtained when it is isolated in the form of its phenylhydrazone, which is only very sparingly soluble. This may then be decomposed with benzaldehyde or formaldehyde. *r*-Galactose melts at 143—144° (corr.) and the *d*-compound at 165·5° (corr.). The inactive galactose appears to be a true racemic compound. One part of *r*-galactose dissolves in 24·93 parts of 85 per cent. alcohol at 38·5°, and 1 part of *d*-galactose in 166·67 parts at the same temperature.

l-Galactose may be obtained by the action of yeast on the racemic compound.

r-*Galactose phenylmethylhydrazone*, $C_{13}H_{20}O_5N_2$, is sparingly soluble in most organic solvents and melts at 183°. J. J. S.

Composition of Manna. CHARLES TANRET (*Bull. Soc. chim.*, 1902, 27, [iii], 947—963).—The manna exuded by *Fraxinus ornus* and *F. rotundifolia* contains, in addition to small amounts of resin and inorganic salts, mannitol, 40—55; lævulose, 2·5—3·4; dextrose, 2·2—3; *manneotetrose*, 12—16; and *manninotriose*, 6—16 per cent. The two latter occur in the portion soluble in 70 per cent. alcohol and are isolated therefrom by fractional crystallisation from

90 per cent. alcohol. *Manneotetrose*, $C_{24}H_{42}O_{21}$, separates from water with 4·5 mols. of the solvent, and from alcohol in monoclinic crystals (with $4H_2O$) [$a:b:c = 1·0512:1:0·4213$; $\gamma = 91°46'$] and melts at 100°. One part dissolves at 13° in 0·75 part of water, and at 15° in 14, 55, and 300 parts of 60, 70, and 80 per cent. alcohol respectively. It has $[\alpha]_D$ +150°. The sugar does not reduce Fehling's solution, but is hydrolysed by acetic acid, water, and the enzymes invertase, emulsin, and diastase into lævulose and *manninotriose*, and by dilute mineral acids into lævulose, 1 mol., dextrose, 1 mol., and galactose, 2 mols. With ammoniacal lead acetate, the compound $C_{24}H_{34}O_{21}Pb_4$ is formed, and with baryta water and alcohol the derivative $2C_{24}H_{42}O_{21},3BaO$. The *acetyl* derivative, $C_{24}C_{26}O_{21}Ac_{16}$, is amorphous, insoluble in water, and has $[\alpha]_D$ +127° in acetic acid, and +125° in alcoholic solution.

Manninotriose, $C_{18}H_{32}O_{16}$, separates from boiling ethyl alcohol in spheres and from methyl alcohol in baton-shaped masses. It is miscible with water in all proportions; one part dissolves at 15° in 60 and 130 parts of 85 and 90 per cent. alcohol respectively, in 200 parts of boiling absolute alcohol, and at 20° in 35 parts of methyl alcohol. It sinters at 140°, melts at 150°, and has $[\alpha]_D$ +167°. The reducing power, compared with that of dextrose, is 0·33 : 1. It is slowly fermented by yeast and is hydrolysed by dilute mineral acids, but not by enzymes. Ammoniacal lead acetate gives a precipitate of the composition $C_{18}H_{24}O_{16}Pb_4$, and with baryta and alcohol a barium compound of the composition $C_{18}H_{32}O_{16},BaO$ is produced. The *acetyl* derivative, $C_{18}H_{20}O_{16}Ac_{12}$, is non-crystalline and has $[\alpha]_D$ +131° in acetic acid and +135° in alcoholic solution.

When oxidised with bromine, the monobasic *manninotrionic acid*, $C_{18}H_{32}O_{17}$, is formed; this is amorphous and furnishes amorphous barium and calcium salts, does not reduce Fehling's solution, and is hydrolysed by acids into gluconic acid, 1 mol., and galactose, 2 mols.

T. A. H.

Meta- and Para-saccharin. HEINRICH KILIANI and HEINRICH NAEGELL (*Ber.*, 1902, **35**, 3528—3533).—The details of the preparation of meta- and para-saccharin (Abstr., 1893, i, 546) have been improved, and an attempt has been made to determine the constitution of each by oxidation with hydrogen peroxide. Calcium meta-saccharinate, when oxidised with hydrogen peroxide, yields *meta-saccharopentose*, $C_5H_{10}O_4$, which crystallises from a mixture of methyl alcohol and ether in plates, melts at 95°, is extremely hygroscopic, and optically inactive. Neither the *phenylhydrazone* nor the *acid* and its *lactone*, which is formed by the oxidation of the pentose by bromine, were obtained in a crystalline condition. The constitution of meta-saccharinic acid is probably $OH·CH_2·[CH·OH]_2·CH_2·CH(OH)·CO_2H$.

The oxidation of para-saccharin with nitric acid yielded no definite product.

R. H. P.

Starch Iodide. LAUNCELOT W. ANDREWS and HENRY MAX GOETTSCH (*J. Amer. Chem. Soc.*, 1902, **24**, 865—881).—A clear solution of starch dissolves iodine to such an extent that, after allowing for

the iodine dissolved by the water alone, the proportion present can be represented by the formula $(C_6H_{10}O_5)_{12}I$. When starch is heated at 100° for a short time with excess of iodine, so much is taken up as corresponds with the formula $(C_6H_{10}O_5)_{12}I_2$. When blue starch iodide solution is heated at 100° for some time, a colourless solution is obtained which contains most of the iodine in the form of an organic iodide, but part of it is present as hydrogen iodide.

When blue starch iodide solution is shaken with chloroform, the iodine is at first quickly removed from the aqueous layer, but after the major portion has been withdrawn the remainder is not easily extracted. The vapour tension (determined by passing a current of air through the solution and ascertaining the loss of iodine and water) of iodine from starch iodide solution is fairly high at first, but after the first portion of the iodine has been removed the vapour tension becomes very minute.

The authors regard starch iodide as a dissociable compound and not as a solution of iodine in starch. This view is supported by the following facts. (*a*) Dry starch and iodine form a brown substance; the presence of water is essential for the formation of the blue colour. (*b*) When heated, the blue colour is destroyed without loss of iodine; this is as would be expected if dissociation takes place. (*c*) Increase of temperature of the system aqueous starch-chloroform causes a larger proportion of iodine to pass into the chloroform phase. (*d*) The low vapour tension of iodine in starch iodide solution indicates that the iodine is chemically united.

J. McC.

Decomposition of Ammonium Chloride in presence of Calcium Carbide. ROBERTO SALVADORI (*Studi Sassaresi*, 1901, 1, 106—108).—The reaction between ammonium chloride and calcium carbide is not a simple one but gives rise to many different compounds; for a definite temperature and a particular concentration of the reacting substances, however, it can be expressed by an equation which, for equivalent quantities of the two reagents and at temperatures between 200° and 300°, is as follows: $3CaC_2 + 6NH_4Cl = 2NH_2Me + 2NH_2{\cdot}NHMe + C_2H_2 + 3CaCl_2$.

In general, at relatively low temperatures, hydrazine- and amine-compounds and acetylene are formed; at higher temperatures, the amines increase and the acetylene decreases, whilst methane is also formed, carbon deposited, and a strong odour of pyridine observed. Among the hydrazine derivatives produced, especially at high temperatures, is a small quantity of phenylhydrazine. The calcium present is always completely converted into chloride.

T. H. P.

Action of Cyanogen Chloride on Methylamine. L. KAESS and J. GRUSZKIEWICZ (*Ber.*, 1902, **35**, 3598—3600).—In cold ethereal solution, cyanogen chloride interacts with methylamine (2 mols.), forming principally *s*-dimethylguanidine hydrochloride (contrast Cahours and Cloez, *Compt. rend.*, 1854, **38**, 358); some methylcyanamide is also formed. The action is thus strictly analogous to that between cyanogen iodide and methylamine (Erlenmeyer, *Ber.*, 1881, **14**, 1868).

W. A. D.

Preparation of Tetramethylammonium. WILHELM PALMAER (*Zeit. Elektrochem.*, 1902, 8, 729—731).—A solution of tetramethylammonium chloride or hydroxide (containing about 2 per cent. of chloride) in liquid ammonia is electrolysed with platinum electrodes. Blue striæ are seen at the cathode, which are probably a solution of tetramethylammonium. Liquid ammonia dissolves about 0·06 gram-equivalent of the chloride per litre, and slightly more of the hydroxide. T. E.

New Hydroxyamino-acid. CARL NEUBERG and H. WOLFF (*Chem. Centr.*, 1902, ii, 841; from *Centr. med. Wiss*, 40, 530).—By the combination of hydrogen cyanide with chitosamine, a nitrile is formed which, on hydrolysis, yields a *hydroxyamino-acid.* This acid is a homologue of Fischer's *iso*serine, and like that compound forms a characteristic basic copper salt. E. W. W.

Synthesis of Serine, *l*-Glucosaminic Acid, and other Hydroxyamino-acids. EMIL FISCHER and HERMANN LEUCHS (*Ber.*, 1902, 35, 3787—3805. Compare Abstr., 1902, i, 268).—α-Amino-γ-hydroxyvaleric acid, $OH\cdot CHMe\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, prepared from aldol-ammonia and hydrogen cyanide, crystallises from hot dilute alcohol in colourless plates, melts and decomposes at about 212° when rapidly heated, has a sweet taste, and is neutral, but dissolves copper oxide with formation of a deep blue solution; the *copper* salt, $Cu(C_5H_{10}O_3N)_2$, crystallises in hexagonal tablets. The *lactone*, $C_5H_9O_2N$, is a colourless, hygroscopic, basic liquid, which gradually changes to a solid condensation product; the *hydrochloride*, $C_5H_9O_2N,HCl$, crystallises from alcohol in glistening flakes or minute prisms and melts with decomposition at 198—200° (corr.). *Di-β-hydroxypropyldiketopiperazine*, $OH\cdot CHMe\cdot CH_2\cdot CH{<}{\substack{CO\cdot NH\\ NH\cdot CO}}{>}CH\cdot CH_2\cdot CHMe\cdot OH$, the condensation product referred to above, crystallises from hot alcohol in pointed plates, melts at 223—225° (corr.), has no odour, cannot be distilled under 10 mm. pressure and is readily soluble in water, giving a solution which has a neutral reaction and does not become blue when boiled with precipitated copper oxide. The *phenylcarbimide* compound of the lactone crystallises from hot water in colourless needles or prisms, melts at 165—166° (corr.), and dissolves readily in sodium hydroxide. The acid is reduced by hydrogen iodide and phosphorus to α-amino-n-valeric acid.

Galaheptosamic acid, $OH\cdot CH_2\cdot[CH(OH)]_4\cdot CH(NH_2)\cdot CO_2H$, from galactosimine-ammonia and hydrogen cyanide, crystallises in microscopic, rectangular tablets or prisms, dissolves in 30 parts of hot water or 962 parts of water at 20°, becomes brown at 210°, and melts at 240° (corr.) liberating gas; it dissolves in sodium hydroxide, or in excess of ammonia, but the ammonium salt is decomposed on heating the solution; it also dissolves in 5 per cent. hydrochloric acid to a dextrorotatory solution, $[\alpha]_D$ +11·23° at 20°. The *copper* salt, $(C_7H_{14}O_7N)_2Cu,2H_2O$, crystallises from about 800 parts of hot water in small, blue granules and becomes anhydrous at 130°.

l-*Glucosamic acid*, $C_6H_{13}O_6N$, from arabinosimine and hydrogen

cyanide, crystallises from water in colourless, rectangular tablets or prisms or in needles and decomposes without melting at 250°. It has a specific rotatory power equal and opposite to that of the *d* compound, but is distinctly less soluble, possibly owing to some impurity in the *d*-acid. The *racemic* acid is much less soluble than the active acids and dissolves in 57·4 parts of water at 20°. T. M. L.

Oxidation of Lysine. GOSWIN ZICKGRAF (*Ber.*, 1902, **35**, 3401—3402).—Lysine sulphate (5 grams) was oxidised in dilute aqueous solution by barium permanganate (20 grams) at 70°; a very small quantity of oxalic acid was obtained as barium oxalate; glutamic acid (?) was also found in very small amount. Glutaric acid formed the major portion of the acids present. In a special experiment, in which the vapour given off during the oxidation was collected, it was shown that hydrogen cyanide acid was produced.

K. J. P. O.

Aminoacetone. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1902, **35**, 3805—3811. Compare Gabriel and Pinkus, Abstr., 1893, i, 734).—*Aminoacetone hydrochloride*, $CH_2Ac\cdot NH_2,HCl$, forms hygroscopic, rhombic tablets and melts at 75°. By the action of potassium hydroxide, it is converted into a *base*, $C_6H_{10}N_2$, formed by elimination of $2H_2O$ from 2 mols. of aminoacetone; this crystallises from ethyl acetate in colourless, octahedral crystals, melts at 115—116°, and is reconverted into aminoacetone salts when boiled with mineral acids; the *oxalate* crystallises in needles and melts and decomposes at 176—177°; the *platinichloride*, $(C_6H_{10}N_2)_2,H_2PtCl_6$, forms orange-red, hexagonal or rhombic plates and does not melt when heated, but blackens, evolving an odour suggestive of dimethylpyrazine; the *aurichloride*, $C_6H_{10}N_2,HAuCl_4$, crystallises in sulphur-yellow, flat prisms, with $1H_2O$, and begins to decompose at 50°; the *picrate*, $C_6H_{10}N_2,2C_6H_3O_7N_3$, separates from alcohol in needles, sinters at about 160°, and melts with frothing at 163—168°. The base is regarded as a *dimethyldihydropyrazine*, $N{<}{\begin{matrix}CMe\cdot CH_2\\ CH_2\cdot CMe\end{matrix}}{>}N$. T. M. L.

Dithiourethanes. JULIUS VON BRAUN [and, in part, K. RUMPF] (*Ber.*, 1902, **35**, 3368—3388. Compare Abstr., 1902, i, 271).—For the preparation of dithiourethanes two new methods are proposed; ethyl chlorothiocarbonate yields, with secondary amines in ethereal solution, dialkyl dithiourethanes; in the second method, which is nearly of universal applicability, an amine (2 mols.), carbon disulphide (1 mol.), and an alkyl iodide are allowed to interact in alcoholic solution. The first two substances yield a salt of a dithiocarbamic acid, which then reacts with the alkyl iodide (compare Delépine, Abstr., 1902, i, 199, 353, 595).

Dithiourethanes having two alkyl groups, $NRR'\cdot CS_2R$, can be distilled and even heated under pressure without undergoing change. The urethanes of the types $NH_2\cdot CS_2R$, $NHR\cdot CS_2R$, break up on heating into thiocarbimides and mercaptans. This decomposition is of the nature of a dissociation; in one case, propyl mercaptan and benzyl-

thiocarbimide, recombination took place at the ordinary temperature. Attention is drawn to the fact that betaines of the form

$$(CH_2)_x{<}^{NR_3}_{CO-}{>}O$$

undergo a similar decomposition on heating (compare Willstätter, Abstr., 1902, i, 266). With urethanes of the last-mentioned type, when the nature of the alkyl group attached to the sulphur permits it, intramolecular condensation takes place with the formation of a five-membered ring.

S-*Ethyl*-N-*dipropyldithiourethanes*, $NPr_2{\cdot}CS_2Et$, is prepared by mixing together ethereal solutions of ethyl chlorothiocarbonate (1 mol.) (the details of the preparation of which are given) and dipropylamine (2 mols.); dipropylamine hydrochloride immediately separates; the urethane is distilled under reduced pressure, boiling at 170—172° under 28 mm. N-*Dibenzyl*-S-*ethyldithiourethane*, $N(C_7H_7)_2{\cdot}CS_2Et$, is prepared in a similar manner, or by mixing alcoholic solutions of dibenzylamine (2 mols.), carbon disulphide (1 mol.), and ethyl iodide (1 mol.); on adding water, the urethane is precipitated as an oil; it crystallises in white needles melting at 38° and boiling at 280—300° under reduced pressure. *Trimethylurethane*, $NMe_2{\cdot}CS_2Me$, is easily prepared by treating dimethylamine dimethyldithiocarbamate with methyl iodide; it crystallises in lustrous leaflets melting at 47° and is volatile in steam. The same substance is obtained from phenyldimethylthiocarbamide, which combines with methyl iodide forming the *salt*

$$NMe_2{\cdot}C(\colon NPh){\cdot}SMe,HI;$$

the latter is a white, crystalline powder melting at 134—135°; the corresponding *base* is an oil boiling at 154—155° under 12 mm. pressure, and when heated with carbon disulphide yields phenylthiocarbimide and trimethyldithiourethane. The analogously constituted *tripropylurethane*, $NPr_2{\cdot}CS_2Pr$, is an oil boiling at 159—160° under 10 mm. pressure. Both these urethanes are very stable; they can be heated to a high temperature or boiled with acids or alkalis, or with concentrated alcoholic solutions of primary amines, ammonia, or hydroxylamine without change.

S-*Methyldithiourethane*, $NH_2{\cdot}CS_2Me$, prepared from ammonium dithiocarbamate and methyl iodide, is a crystalline powder melting at 42°; S-*allyldithiourethane*, $NH_2{\cdot}CS_2{\cdot}C_3H_5$, is prepared similarly and melts at 32°; S-*benzyldithiourethane*, $NH_2{\cdot}CS_2{\cdot}C_7H_7$, melts at 91°; when freshly prepared, these three substances are odourless, but on keeping exhale a mercaptan-like odour; a complete decomposition into mercaptan and thiocyanic acid takes place when they are distilled. Benzyl mercaptan can easily be prepared by rapidly distilling the urethane under reduced pressure and extracting the thiocyanic acid from the oil which results from the action of water. N-S-*Dimethyldithiourethane*, $NHMe{\cdot}CS_2Me$, prepared from methylamine, carbon disulphide, and methyl iodide, is a yellowish, odourless oil, which boils at 155—156° under 20 mm. pressure; when heated under the ordinary pressure in a current of air, carbon dioxide, or hydrogen, this compound remains unchanged at 155°, but at 163—165° decomposes rapidly into methyl mercaptan and methylthiocarbimide. On the other hand, if the urethane is heated under pressure at 150—180° for several hours, practic-

ally no decomposition occurs. The three last-mentioned urethanes do not react with amines in the cold, but on warming a thiocarbamide is produced owing to decomposition of the urethane into a thiocarbamide; thus dimethyldithiourethane and aniline yield *S*-methylphenylcarbamide (m. p. 114°). S-*Ethyl*-N-iso*amyldithiourethane*,

$$C_5H_{11}\cdot NH\cdot CS_2Et,$$

is a liquid boiling at 167—168° under 15 mm. pressure. N-*Benzyl* S-*propyldithiourethane*, $C_7H_7\cdot NH\cdot CS_2Pr$, is prepared by treating benzylamine benzyldithiocarbamate with propyl iodide in the presence of alcohol; the crystals melt at 63°; on attempting to distil this urethane, it decomposes completely into benzyl mercaptan and benzylthiocarbimide, the first-mentioned substance distilling over at a temperature of 70—120°, the other at 240—260°.

N-*Methylcyclohexyl*-S-p-*nitrobenzyldithiourethane*,

$$C_7H_{13}\cdot NH\cdot CS_2\cdot C_7H_5\cdot NO_2,$$

obtained from 1:3-methyl*cyclo*hexylamine, carbon disulphide, and *p*-nitrobenzyl chloride, melts at 95°, and when warmed yields methyl*cyclo*hexylthiocarbimide.

N-*Phenyl* S-*benzyldithiourethane* is readily prepared by acting on ammonium phenyldithiocarbamate with alcoholic benzyl chloride and melts at 84° (compare Fromm and Bloch, Abstr., 1899, i, 887). N-*Phenyl*-S-*allyldithiourethane*, $NHPh\cdot CS_2\cdot C_3H_5$, prepared from ammonium phenyl dithiourethane and allyl iodide, is a white, crystalline powder melting at 42°. Attempts at distillation, even under reduced pressure, lead to complete decomposition of these two phenylurethanes.

From bromoacetophenone, *iso*butylamine, and carbon disulphide, a urethane cannot be obtained, but the ring compound,

$$CS<\begin{matrix}N(C_4H_9)\cdot CPh \\ S\text{———}CH\end{matrix},$$

is formed which melts at 83°. *iso*Amylamine, carbon disulphide, and ethylene dibromide yield a yellow, odourless liquid boiling at 155—157° under 12 mm. pressure, which is probably a thiazoline derivative, $CS<\begin{matrix}N(C_5H_{11})\cdot CH_2 \\ S\text{———}CH_2\end{matrix}$. Ethylamine, carbon disulphide, and ethyl α-bromo*iso*butyric acid give an odourless liquid, which appears to be the compound $NHEt\cdot CS_2\cdot CMe_2\cdot CO_2Et$. When distilled under reduced pressure, alcohol is eliminated and a yellowish-green, thick oil, $CS<\begin{matrix}NEt\cdot CO \\ S\text{——}CMe_2\end{matrix}$, is obtained; it boils at 122—124° under 10 mm. pressure and when boiled with alcoholic alkalis is converted into α-thiol*iso*butyric acid; the *silver* salt, $AgS\cdot CMe_2\cdot CO_2Ag$, is a powder unchanged by light.

From ammonium phenyldithiocarbamate and ethyl bromoacetate, the *urethane*, $NHPh\cdot CS_2\cdot CH_2\cdot CO_2Et$, is obtained; it is a crystalline powder melting at 63°, which when heated at 100—110° loses alcohol and is converted into a compound melting at 188°, this being very probably a tetrahydrothiazole derivative, $CS<\begin{matrix}NPh\cdot CO \\ S\text{——}CH_2\end{matrix}$. Attempts to synthesise this compound by the action of carbon disulphide on diphenyl*iso*dithiohydantoin were unsuccessful.

Ethyl α-bromo*iso*butyrate and ammonium phenyldithiocarbamate do not give a urethane, but yield directly the ring *compound*, $CS<\begin{matrix} NPh\cdot CO \\ S\text{——}CMe_2 \end{matrix}$, which melts at 116°.

The sole product of the interaction of dibenzylamine, carbon disulphide, and bromoacetal, is a compound, $(C_7H_7\cdot N\cdot CS)_2O$, melting at 81°, which probably results from the decomposition of the dibenzylamine dibenzyldithiocarbamate first formed. K. J. P. O.

Dissociation of the Compound of Iodine and Thiocarbamide. HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1902, **24**, 233—239).—Dithiocarbamide di-iodide has already been obtained by McGowan (Trans., 1886, **49**, 195). It can be prepared by adding 5 parts of iodine to 3 parts of thiocarbamide mixed with about 25 parts of water; it separates in colourless, prismatic crystals. When dissolved in water, a yellowish solution is obtained, the colour being due to iodine liberated according to the balanced action $(CSN_2H_4)_2I_2 \rightleftarrows 2CSN_2H_4 + I_2$. The salt is also capable of ionising, according to the equation $(CSN_2H_4)_2I_2 \rightleftarrows (CSN_2H_4)_2^{\cdot\cdot} + 2I'$; this is suggested by the facts that it easily takes part in reactions of double decomposition, that it dissolves free iodine, that it precipitates lead and silver iodides, and that it dissolves mercuric iodide. When the degree of ionisation is diminished, the first balanced action becomes more prominent, and there is a greater amount of iodine liberated. The liberation of iodine is due to the dissociation of the non-ionised part of the substance, because the quantity liberated increases with decreasing ionising power of the solvent. In methyl alcohol, the amount of iodine liberated is greater than in water; in ethyl alcohol it is greater, and in acetone it is greater still. The order of the amounts of iodine liberated is the inverse of the ionising powers of the solvents (Carrara, Abstr., 1897, ii, 471).

When the ionisation in aqueous solution is diminished by the addition of ether, a deepening of the colour of the solution takes place, so also when the ionisation is decreased by the addition of soluble iodides. J. McC.

Arylhydantoins. GUSTAV FRERICHS and G. BREUSTEDT (*J. pr. Chem.*, 1902, [ii], **66**, 231—261. Compare Abstr., 1899, i, 806).—The compounds obtained by the action of potassium hydroxide on the β-arylhydantoins are additive products and not salts of the corresponding hydantoic acids, as, with alkyl haloids, they yield γ-alkylhydantoins.

β-Phenylhydantoin potassium hydroxide crystallises in leaflets. *β-Phenyl-γ-ethylhydantoin* crystallises in delicate, colourless needles, melts at 142°, is easily soluble in warm alcohol, glacial acetic acid, ethyl acetate, or chloroform, and, on distillation with potassium hydroxide, yields ethylamine and phenylglycine. *β-Phenyl-γ-methylhydantoin* crystallises in clusters of colourless leaflets and melts at 185°. *β-Phenyl-γ-propylhydantoin* crystallises in colourless needles and melts at 82—84°. *β-Phenyl-γ-allylhydantoin* crystallises in delicate leaflets

and melts at 117—118°. β-*Phenyl-γ-cetylhydantoin* crystallises in glistening leaflets and melts at 81—82°.

β-p-*Tolyl-γ-methylhydantoin* crystallises in long, delicate needles and melts at 174—175°. β-p-*Tolyl-γ-ethylhydantoin* forms feathery crystals and melts at 139°. β-p-*Tolyl-γ-propylhydantoin* crystallises in long, glistening needles and melts at 124—125°. β-p-*Tolyl-γ-allylhydantoin* crystallises in needles and melts at 125°. β-p-*Tolyl-γ-cetylhydantoin* crystallises in colourless, glistening leaflets and melts at 95°.

β-o-*Tolyl-γ-methylhydantoin* crystallises in delicate needles and melts at 126—127°. β-o-*Tolyl-γ-ethylhydantoin* crystallises in leaflets and melts at 99—100°. β-o-*Tolyl-γ-propylhydantoin* crystallises in delicate leaflets and melts at 71—72°. β-o-*Tolyl-γ-allylhydantoin* forms thick crystals and melts at 67—68°. β-o-*Tolyl-γ-cetylhydantoin* crystallises in glistening leaflets and melts at 58°.

β-m-*Tolylhydantoin* crystallises in colourless, flat needles, melts at 166—167°, and is easily soluble in hot water, alcohol, glacial acetic acid, or ethyl acetate. β-m-*Tolyl-γ-methylhydantoin* crystallises in clusters of delicate needles and melts at 150—151°. β-m-*Tolyl-γ-ethylhydantoin* crystallises in delicate needles and melts at 91—92°. β-m-*Tolyl-γ-propylhydantoin* crystallises in delicate needles and melts at 87—88°. β-m-*Tolyl-γ-allylhydantoin* crystallises in delicate needles and melts at 98—99°. β-m-*Tolyl-γ-cetylhydantoin* crystallises in colourless, glistening leaflets and melts at 78—79°.

β-p-*Ethoxyphenyl-γ-methylhydantoin* crystallises in long, delicate needles and melts at 180—181°. β-p-*Ethoxyphenyl-γ-ethylhydantoin* crystallises in delicate needles and melts at 131°. β-p-*Ethoxyphenyl-γ-propylhydantoin* crystallises in clusters of needles and melts at 121—122°. β-p-*Ethoxyphenyl-γ-allylhydantoin* crystallises in long needles and melts at 127—128°. β-p-*Ethoxyphenyl-γ-cetylhydantoin* crystallises in delicate, glistening leaflets and melts at 100—101°.

By addition of hydrogen bromide to the γ-allylhydantoins in glacial acetic acid solution at 90—100° under pressure, the following have been prepared: β-*Phenyl-γ-bromopropylhydantoin*, which crystallises in groups of needles and melts at 158—159°; β-p-*tolyl-γ-bromopropylhydantoin*, which crystallises in leaflets and melts at 149—150°; β-o-*tolyl-γ-bromopropylhydantoin*, which crystallises in colourless, brittle prisms and melts at 60—61°; β-m-*tolyl-γ-bromopropylhydantoin*, which crystallises in delicate, colourless leaflets and melts at 141—142°, and β-p-*ethoxyphenyl-γ-bromopropylhydantoin*, which crystallises in delicate needles and melts at 167—168°.

The following have been prepared by the action of bromine on the γ-allylhydantoins in cold glacial acetic acid solution: β-*phenyl-γ-dibromopropylhydantoin*, which crystallises in colourless leaflets and melts at 127°; β-p-*tolyl-γ-dibromopropylhydantoin*, which crystallises in leaflets and melts at 124°; β-o-*tolyl-γ-dibromopropylhydantoin*, which forms nodular crystals and melts at 104—105°; β-m-*tolyl-γ-dibromopropylhydantoin*, which crystallises in delicate, matted needles and melts at 77—78°, and β-p-*ethoxyphenyl-γ-dibromopropylhydantoin*, which crystallises in delicate needles and melts at 129—130°.

β-*Bromophenyl-γ-dibromopropylhydantoin*, which crystallises in delicate needles and melts at 153—154°, β-*bromo-m-tolyl-γ-dibromo-*

propylhydantoin, which crystallises in delicate, colourless needles and melts at 117°, and *β-bromo*-p-*ethoxyphenyl-γ-dibromopropylhydantoin*, which crystallises in matted, delicate needles and melts at 155—156°, are formed by the action of an excess of bromine on the γ-allylhydantoins in glacial acetic acid solution.

β-p-*Bromophenylhydantoin*, formed by the action of bromine on β-phenylhydantoin and by the action of chloroacetylurethane on *p*-bromoaniline, crystallises in long, glistening needles and melts at 233—234°.

β-Bromo-m-*tolylhydantoin*, formed by bromination of tolylhydantoin, crystallises in needles and melts at 221—222°. *β-Bromo*-p-*ethoxyphenylhydantoin* crystallises in delicate needles and melts at 230°.

The following new glycinyl ethyl urethanes,

$$CO_2Et \cdot NH \cdot CO \cdot CH_2 \cdot NHR,$$

and β-arylhydantoins are described. m-*Xylylglycinyl ethyl urethane*, [$R = C_8H_9$], crystallises in long, colourless, soft needles and melts at 123—124°; *ψ-cumyl-*, [$R = C_9H_{11}$], crystallises in long, silky needles and melts at 154—155°; o-*methoxyphenyl-*, [$R = C_6H_4 \cdot OMe$], crystallises in clusters of needles and melts at 134—135°; o-*chlorophenyl-*, [$R = C_6H_4Cl$], crystallises in needles and melts at 115°; *β*-m-*xylylhydantoin* crystallises in colourless needles and melts at 146—147°; *β-ψ-cumylhydantoin* crystallises in delicate, colourless leaflets and melts at 190—191°; *β*-p-*methoxyphenylhydantoin* forms leaflets and melts at 196—197°; *β*-p-*chlorophenylhydantoin* crystallises in long needles and melts at 230°; *β*-m-*chlorophenylhydantoin* crystallises in matted needles and melts at 166—167°. G. Y.

Composition of the Ferrocyanides of Zinc. EDMUND H. MILLER and J. L. DANZIGER (*J. Amer. Chem. Soc.*, 1902, **24**, 823—828).—The composition of the potassium zinc ferrocyanides precipitated in different ways (in neutral, acid, or ammoniacal solution with excess of one or other of the reagents) has been determined. The ratio of iron to zinc has been found to vary from 1 : 1·35 to 1 : 1·59. When left for some time in contact with the solution from which it was precipitated, the substance changes in composition in such a way that the proportion of zinc increases. In ammoniacal solution, the salt $Zn_2Fe(CN)_6$ is precipitated, and this is also produced by washing any of the zinc potassium ferrocyanides with concentrated ammonia solution.

In order to find if the zinc potassium ferrocyanides produced are mixtures or definite compounds, an attempt was made to separate them by collecting the first part of the precipitate which settled and then the lighter portion, but these portions were found to have the same composition, showing that no separation had been effected.

It has not been possible to obtain a pure zinc potassium ferrocyanide of the formula $K_2ZnFe(CN)_6$. J. McC.

Solubility of Prussian Blue. GRÉGOIRE WYROUBOFF (*Bull. Soc. chim.*, 1902, **27**, 940—941. Compare Coffignier, Abstr., 1902, i, 664).—It is suggested that when Prussian blue is dissolved in warm hydrochloric acid, a colourless additive compound is formed which, on the addition of water, undergoes dissociation. T. A. H.

Heptanaphthylenes. Wladimir B. Markownikoff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 632—635).—Owing to the publication of a paper by Zelinsky (Abstr., 1902, i, 597), the author points out that he has already carried out investigations on the same subject (Abstr., 1900, i, 579), and refers shortly to some fresh work he has been doing on the optical properties of the methyl*cyclo*hexenes, on the isomerism of the heptanaphthene chlorides, and on a new heptanaphthenol and diheptanaphthene; the results are to be published later in full.

T. H. P.

Ring-system of Benzene. III. Hugo Kauffmann (*Ber.*, 1902, **35**, 3668—3673).—The author discusses his interpretation of the behaviour of benzene derivatives with Tesla rays (see Abstr., 1900, i, 480; 1901, i, 318; 1902, ii, 191). He ascribes the centric, Kekulé, or Claus (as modified by Baeyer) formulæ to various benzene derivatives according to their behaviour under the Tesla rays. R. H. P.

Benzene in Grosny Naphtha and the Chemical Characters of the Latter. Wladimir B. Markownikoff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 635—636).—The fraction boiling below 105° of Grosny naphtha contains 3·79 per cent. of benzene, that is, about six times as much as was found by the author in a Baku naphtha of sp. gr. 0·739 (Abstr., 1897, i, 329). It is hence possible, after careful fractionation, to prepare nitrobenzene from Grosny naphtha. This naphtha contains less hexanaphthene but more heptanaphthene and methyl*cyclo*pentane than that obtained from Baku. T. H. P.

Styrenes. III. August Klages [and Heino Hahn] (*Ber.*, 1902, **35**, 3506—3510. Compare Abstr., 1902, i, 666).—The magnesium allyl iodide derivatives of the ketones, when treated with dry ammonia, yield additive products which, when decomposed by water, furnish alkylated styrenes. The *compound* $COPhMe,MgCH_3I,2NH_3$ is produced by passing ammonia gas over the powdered magnesium derivative, the absorption of the gas being attended by an appreciable rise of temperature; β-allylbenzene is produced from the ammonia compound by the action of water.

Phenylmethylethylcarbinol, CPhMeEt·OH, produced by the interaction of acetophenone and magnesium ethiodide in the cold, is a colourless oil having a faint odour and boiling at 102° under 14 mm. pressure; it has a sp. gr. 0·9815 at 22°/4° and n_D 1·5158 at 22°. The corresponding *chloride* is a colourless oil having an odour of cymene.

1-Metho-1′-propenylbenzene (β-phenyl-Δ^{β}-butylene) may be obtained either by heating the chloride with pyridine or by treating the magnesium derivative with ammonia and decomposing the additive product with dilute sulphuric acid. The ammonia compound of the magnesium propiodide derivative of acetophenone does not furnish a hydrocarbon, but gives rise to phenylmethylpropylcarbinol, the chloride of which, on heating with pyridine, yields 1-metho-1′-butenylbenzene (β-phenyl-Δ^{β}-amylene). This hydrocarbon forms a *dibromide*, CMePhBr·CHEtBr, a colourless oil of high boiling point which has an odour of peppermint.

1-Metho-1′-butenylbenzene, on reduction with sodium and ethyl alcohol, furnishes *sec.*amylbenzene (b. p. 191—193°).

The physical properties of the hydrocarbons described in this and the preceding communications on substituted styrenes are displayed in tabular form. G. T. M.

Influence of the Cathode Material on the Electrolytic Reduction of Aromatic Nitro-compounds. WALTHER LÖB (*Zeit. Elektrochem.*, 1902, **8**, 778—779).—Nitrobenzene and its derivatives behave similarly when submitted to electrolytic reduction. With nickel or mercury cathodes, azoxy-compounds together with azo-compounds are formed. Lead, zinc, tin, and copper cathodes yield mainly azo- and hydrazo-compounds, whilst the addition of copper powder to the electrolyte leads to the formation of the amino-derivative. Whilst the different compounds behave on the whole in the same way, they differ in various particulars. T. E.

Sulphone of Di*cyclo*pentadiene. JOHANNES BOES (*Chem. Centr.*, 1902, ii, 32; from *Apoth.-Zeit.*, **17**, 340—341).—The formation of sulphur dioxide when benzene is washed with sulphuric acid is mainly due to the presence of di*cyclo*pentadiene. This compound is more readily attacked by sulphuric acid than either coumarone or indene. The concentrated acid acts explosively and causes combustion, whilst by the action of dilute acid a soluble and an insoluble resin are formed. The latter is not a polymeride of *cyclo*pentadiene. The quantity of the soluble resin which is formed increases with the concentration of the acid; it consists of the *sulphone*, $C_{20}H_{22}O_2S$, and forms a dry mass which can be powdered. The products obtained by the dry distillation of the resin do not contain *cyclo*pentadiene and in this respect, therefore, *cyclo*pentadienesulphone differs from coumaronesulphone. E. W. W.

Sulphonation of 1 : 8-Dinitronaphthalene. O. ECKSTEIN (*Ber.*, 1902, **35**, 3403—3404).—Although at the ordinary temperature both 1 : 8- and 1 : 5-dinitronaphthalene are converted by fuming sulphuric acid into nitronitrosonaphthols, at a higher temperature (140°) the 1 : 5-compound is untouched by fuming sulphuric acid containing 20 per cent. of anhydride, whereas the 1 : 8-dinitronaphthalene is completely transformed into a sulphonic acid. The *barium* salt, $[(NO_2)_2C_{10}H_5\cdot SO_3]_2Ba,5H_2O$, crystallises in yellowish-brown needles, very soluble in boiling water. The *ferrous* salt forms anhydrous, microscopic needles; the *silver* salt is sparingly soluble. The esters are very easily hydrolysed. This compound appears to be identical with that obtained by Cleve and Hellström by nitrating 1-nitronaphthalene-6-sulphonic acid.

It is found that 1 : 5-dinitronaphthalene can be completely freed from the isomeric 1 : 8-compound by treatment with fuming sulphuric acid. K. J. P. O.

Pyrogenetic Preparation of Diphenyl by the Electric Current. WALTHER LÖB (*Zeit. Elektrochem*, 1902, **8**, 777—778. Compare Abstr., 1901, ii, 371).—The carbon filament of an incandescent

electric lamp is heated to redness in the vapour of benzene boiling on the water-bath. In 4 hours, 7·5 to 8 grams of pure diphenyl and a small quantity of diphenylbenzene are produced. Platinum or nickel wire may be used in place of the carbon filament. T. E.

Action of Aqua Regia on Anilides and Homologous Derivatives. Antonio Verda (*Gazzetta*, 1902, **32**, ii, 20—21).—The action of hydrochloric acid and nitric acid on *o*-acetotoluidide yields a reddish-brown, oily product, probably containing nitrocresol, and a *dichloroacetotoluidide*, which crystallises in white plates melting at 154°.

The interaction of hydrobromic acid, nitric acid, and *o*-acetotoluidide yields a *dibromoacetotoluidide*, crystallising in slender, white needles which melt at 199°. With 6 parts of hydrobromic acid and 1·5 of nitric acid, acetotoluidide yields the 5-bromoacetotoluidide melting at 156—157°.

Similar products are obtained, although not so readily, with *p*-acetotoluidide.

Succinanilide, when treated with hydrochloric and nitric acids, yields a *tetrachlorosuccinanilide*, which is soluble in alcoholic potassium hydroxide, from which water precipitates it as a white, crystalline powder melting at 215°.

In all these cases it is seen that no nitro-group has entered the molecule, but with α-acetonaphthalide, in which the influence of the amino-group is less on account of the double nucleus of the molecule, a nitro-group goes in. Thus, when this compound is treated with hydrochloric acid and nitric acid, it yields a *chloronitroacetylnaphthylamine*, which crystallises from alcohol in shining, yellow needles melting at 216°, and when treated with concentrated potassium hydroxide solution is decomposed into ammonia and chloronitronaphthol. If hydrobromic acid is used in place of hydrochloric acid, 3 : 8 dibromo-α-acetonaphthalide is obtained. T. H. P.

Control Experiments with Chloro-*m*-toluidines and Chloro-*m*-aminobenzoic Acids. Eugen Bamberger and Josef de Werra (*Ber.*, 1902, **35**, 3711—3720).—The results described in another paper (this vol., i, 25) not being in harmony with results obtained by other authorities, the authors have repeated most of this earlier experimental work, and have proved beyond doubt that the three chloro-*m*-toluidines and their derivatives obtained by the action of hydrochloric acid on *m*-tolylhydroxylamine have the following constitutions:

Chlorine =	6.	2.	4.
Chloro-3-toluidine	83·5—84·1°	—	—
Chloro-3-acetotoluidides ...	91·2—91·7°	133—134°	—
Chloro-3-acetylaminobenzoic acids	215—215·5°	207—207·5°	264·5—265·5°
Chloro-3-aminobenzoic acids	188—188·5°	160·5—161	216—217°

The 6-chloro-derivatives are identical with those described by Gold-

schmidt and Hönig and by Reverdin and Crépieux. The former authorities have given the melting point of chlorotolylphenylthiocarbamide as 108—109° instead of 132·5—133°.

The compound described by Griess as 2-chloro-3-aminobenzoic acid is really the 6-chloro-derivative, which is also identical with the acid described by Hübner and Biedermann (*Annalen*, 1868, **147**, 264) as melting at 212° (instead of 188°).

4-Chloro-3-aminobenzoic acid is identical with the compound described by Griess and by Hübner and Biedermann as melting at 212°. The constitution is established by the synthesis from Gattermann and Kaiser's 4-chloro-3-acetotoluidide (Abstr., 1886, 49).

J. J. S.

4-*m*-Xylidine-5-sulphonic Acid. ALFRED JUNGHAHN (*Ber.*, 1902, **35**, 3747—3767. Compare Armstrong and Wilson, Proc., 1900, **16**, 229).—4-m-*Xylidine-5-sulphonic acid* [$Me_2 : NH_2 : SO_3H = 1 : 3 : 4 : 5$] may be obtained by the following methods: (*a*) when *m*-xylene-4-sulphonamic acid (Abstr., 1898, i, 479) is heated for a short time at 220—230°; (*b*) when *m*-xylidine is added to boiling chlorosulphonic acid. The yield in this case is small, as the chief product is the isomeric 6-sulphonic acid, which may be removed by the aid of its readily soluble barium salt; (*c*) when the acid sulphate of *m*-xylidine is heated for 2·5—3 hours at 210—230° under reduced pressure; (*d*) when the normal sulphate of the base is heated in a similar manner or when the sulphate is heated with four times its weight of *m*-xylidine.

The acid crystallises from water in anhydrous, rhombic plates; its solubility in water at 100° is 1 in 28·5. The sulphonic acid group is removed when the acid is heated at 150—155° for 1·5 hours with concentrated hydrochloric acid. The *potassium* and *sodium* salts are anhydrous and dissolve in hot water, the *barium* salt crystallises with $2H_2O$ in large, quadratic plates and is very characteristic. The *lead* and *silver* salts are moderately soluble in hot water.

4-*Diazo*-m-*xylene-5-sulphonic acid* crystallises from warm water in truncated prisms, which decompose when heated. 4-*Bromo*-m-*xylene-5-sulphonic acid*, obtained by warming the diazo-acid with hydrobromic acid, crystallises in colourless needles and is soluble in water or alcohol. The yield is not good, as several bye-products are formed at the same time. The *barium* salt is anhydrous, and the *sodium* salt contains $1H_2O$. The *chloride*, $C_6H_2Me_2Br·SO_2Cl$, crystallises from light petroleum in pale yellow plates melting at 75°, the *amide* crystallises from alcohol in colourless prisms melting at 158°, and the *anilide* in colourless needles melting at 179°. The isomeric 4-*bromo*-m-*xylene*-6-*sulphonanilide* melts at 152°. When the amide (m. p. 158°) is reduced with sodium amalgam and alcohol, it yields *m*-xylene-5-sulphonamide melting at 135·5 (compare Armstrong and Wilson, *loc. cit.*).

6-*Nitro*-4-m-*xylidine*-5-*sulphonic acid* crystallises in colourless needles containing $1H_2O$ and when boiled with hydrochloric acid is readily hydrolysed to 6-nitro-1 : 3 : 4-xylidine melting at 123° (Abstr., 1884, 1011). The *potassium* salt (with $1H_2O$), and the *barium*, *lead*, and *silver* salts are moderately soluble in water.

4-*Diazo-6-nitro* m-*xylene-5-sulphonic acid* crystallises from warm water in reddish coloured needles which are insoluble in alcohol or ether.

4-*Hydroxy*-m-*xylene-5-sulphonic acid*, obtained when 4-diazo-*m*-xylene-5-sulphonic acid is heated with water, is readily soluble in water or alcohol. Its *sodium* salt crystallises with $1H_2O$; the *potassium* salt is anhydrous, and the *barium* salt contains $2H_2O$. The acid is identical with Jacobsen's 4-hydroxy-*m*-xylene-*a*-sulphonic acid (*Annalen*, 1879, **195**, 283), although the barium salt is described as being anhydrous. Dilute solutions of the acid and its salts gave a deep blue coloration with ferric chloride. 4-*Ethoxy*-m-*xylene-5-sulphonic acid*, obtained by the action of absolute alcohol on the diazo-compound at 120—125°, is readily soluble in water, and is accompanied by a nitrogen-free compound which crystallises in long needles melting at 156°. The *potassium* salt, $C_{10}H_{13}O_4SK$, is soluble in hot water, as are also the *barium*, *lead*, and *silver* salts.

4 : 6-*Diamino*-m-*xylene-5-sulphonic acid* crystallises from water in long needles and gives no coloration with ferric chloride in the cold. The *potassium* salt is anhydrous, and the *barium* salt contains $1H_2O$.

4-Diazo-*m*-xylene-5-sulphonic acid reacts with an alkaline solution of β-naphthol, yielding an orange-coloured *dye*,

$$C_{18}H_{15}O_4N_2SNa,3H_2O,$$

which crystallises in plates very sparingly soluble in cold water. The *acid* $C_{18}H_{16}O_4N_2S$ crystallises in golden, microscopic plates. The diazo-compound also reacts with alkaline solutions of resorcinol, yielding a yellow *dye* in the form of a sodium salt. The corresponding *acid*, $C_{14}H_{14}O_5N_2S$, crystallises in reddish-brown plates.

4-Diazo-6-nitro-*m*-xylene-5-sulphonic acid and β-naphthol yield a *dye*, $C_{18}H_{15}O_6N_3S,5H_2O$, which crystallises in long, brick-red needles. When dehydrated, it assumes a black, metallic lustre and yields a yellow, gelatinous sodium salt. J. J. S.

Stereochemistry of Nitrogen. ALBERT REYCHLER (*Bull. Soc. chim.*, 1902, **27**, [iii], 974—979).—Bischoff's view of the arrangement of the affinities of quinquevalent nitrogen (Abstr., 1890, i, 1330) is adopted with the additions that the superficial angles of the system need not all be equal and 120° and that between the central nitrogen atom and its attached groups the distances need not be all equal. It is shown that this view explains satisfactorily syntheses such as those of Wedekind (Abstr., 1899, i, 353) which may be generally represented thus:

$$NRR'R'' + R'''I \rightarrow NRR'R''R'''I \leftarrow NRRR''' + R''I,$$

and it postulates the existence in the case of the types NR_4I and $NR_3R'I$ single in active forms only, for the type $NR_2R_2'I$ two inactive forms, and for the type $NR_2R'R''I$ one inactive form and an enantiomorphic pair, and for the type $NRR'R''R'''I$ six active forms in three enantiomorphic pairs. T. A. H.

Stereochemistry of Nitrogen and the Rotatory Power of β-Naphthylmethylethylamine *d*-Camphorsulphonate. ALBERT REYCHLER (*Bull. Soc. chim.*, 1902, **27**, [iii], 979—982. Compare

preceding abstract).—β-Naphthylmethylethylamine *d*-camphorsulphonate dissolved in a mixture of 9 parts of ethyl acetate and 1 part of alcohol has $[\alpha]_D$ $+32°$ and in absolute alcohol $+28°$ at 20°; these values remain constant after two fractional crystallisations. β-Naphthyldimethylamine and β-naphthyldiethylamine *d*-camphorsulphonates have $[\alpha]_D$ $+35°$, $+30°$ and $+27°$, $+26.5°$ respectively at the same temperatures and in the same solvents. The absence of any separation into oppositely active forms in the case of the β-naphthylmethylethylamine salt by crystallisation leads the author to suggest that this substance may not be a true quaternary ammonium salt (compare Wedekind, *Chem. Centr.*, 1900, ii, 555). T. A. H.

β-Naphthalenesulphonic Derivatives of Amino-acids. Emil Fischer and Peter Bergell (*Ber.*, 1902, **35**, 3779—3787).—The β-naphthalenesulphonic derivatives can be advantageously used for isolating easily-soluble amino-acids.

β-Naphthalenesulphoglycine, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH_2 \cdot CO_2H$, crystallises from hot water in pointed, anhydrous flakes, sinters at 151°, and melts at 159° (corr.); it dissolves in 2670 parts of water at 20° and in about 90 parts of boiling water, and is hydrolysed by heating with hydrochloric acid for 3 hours at 110°; the *copper* salt is very slightly soluble in water and crystallises in minute, glistening, blue flakes; the *ethyl* ester, prepared by means of absolute alcohol and hydrogen chloride, crystallises in minute needles, melts at 74° (corr.), and is soluble in alkalis without undergoing hydrolysis.

r-*β-Naphthalenesulphoalanine*, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot CHMe \cdot CO_2H$, crystallises in minute needles and melts at 152—153° (corr.); the *copper* salt is sparingly soluble in hot water and separates in minute, greenish-blue crystals.

β-Naphthalenesulpho-d-*alanine* crystallises from hot water in minute, hydrated needles, which sinter at 62° and melt at 79—81° (corr.); the anhydrous substance sinters at 117° and melts at 122—123°; the *ethyl* ester forms long, colourless, hydrated needles which melt at 78°; the anhydrous substance melts at 90.5° (corr.).

r-*β-Naphthalenesulpholeucine*, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH(C_4H_9) \cdot CO_2H$, crystallises from hot dilute alcohol in colourless, glistening flakes, melts at 145—146° (corr.), and dissolves in about 500 parts of hot water. The *active* compound, from *l*-leucine, crystallises from 120 parts of 20 per cent. alcohol in thin prisms, sinters at 60°, melts at 68° (corr.), and dissolves in about 400 parts of hot water.

r-*β-Naphthalenesulphophenylalanine*,

$$C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph,$$

crystallises from water in needles, melts at 143—144° (corr.), and dissolves in about 500 parts of hot water,

Active *β-naphthalenesulpho-α-pyrrolidinecarboxylic acid*,

$$C_{10}H_7 \cdot SO_2 \cdot N{<}\begin{matrix} CH_2 \text{———} CH_2 \\ CH(CO_2H) \cdot CH_2 \end{matrix},$$

crystallises from hot, dilute alcohol or from water in long, thin flakes with $1H_2O$; the hydrate sinters at 80°, and melts at 133.7° (corr.), and the dry substance melts at 138° (corr.); it dissolves in about 130 parts of hot water.

β-Naphthalenesulphoserine, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH(CH_2 \cdot OH) \cdot CO_2H$, crystallises from water with or without water of crystallisation ($1 \cdot 3H_2O$), but from hot alcohol it separates in anhydrous needles; it melts at 214° (corr.) and dissolves in about 70—80 parts of hot water; unlike most of the similar derivatives, it is only very slightly soluble in cold alcohol.

β-Naphthalenesulphohydroxy-a-pyrrolidinecarboxylic acid crystallises from hot water in thin flakes with $1H_2O$, sinters at 86°, and melts at 91—92° (corr.) to a brown oil.

β-Naphthalenesulphogaluheptosaminic acid,

$$C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH(CO_2H) \cdot [CH \cdot OH]_4 \cdot CH_2 \cdot OH,$$

crystallises in minute needles, melts at 201° (corr.), and dissolves readily in hot water.

β-Naphthalenesulphoglycylglycine,

$$C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H,$$

crystallises from hot water with $1H_2O$, or from alcohol, and melts at 180—182° (corr.), dissolves in 1515 parts of water at 20°, and in 45 parts of hot water; the *copper* salt separates in microscopic, blue needles or prisms with $1H_2O$. T. M. L.

Action of Hydrochloric Acid on *m*-Tolylhydroxylamine. EUGEN BAMBERGER [with LEON TER-SARKISSJANZ and JOSEF DE WERRA] (*Ber.*, 1902, **35**, 3697—3710).—Finely-divided *m*-tolylhydroxylamine is gradually added to a solution of hydrogen chloride saturated at −8 to −10° and the mixture allowed to remain in an ice-chest for seven days. The products consist of *m*-azoxytoluene, *m*-toluidine, 3-amino-6-cresol (compare Abstr., 1884, 900), and a mixture of three chloro-*m*-toluidines, namely, 6-chloro-3-toluidine in largest quantity (compare Goldsmith and Hönig, Abstr., 1887, 363; Reverdin and Crépieux, *Ber.*, 1900, **33**, 2503), 2-chloro-3-toluidine, yielding an acetyl derivative melting at 132° (compare Wynne and Greeves, Proc., 1895, **11**, 151), and 4-chloro-3-toluidine, the acetyl derivative of which, when oxidised with permanganate, yields 4-*chloro*-3-*acetylaminobenzoic acid* melting at 264·5—265·5°.

6-Chloro-3-toluidine crystallises from light petroleum in long, colourless needles melting at 83·5—84·1° and readily soluble in most organic solvents. A drop of nitrite solution added to a concentrated sulphuric acid solution of the base produces a deep violet-red coloration. The hydrochloride, nitrate, and especially the sulphate, are sparingly soluble in water. The acetyl derivative melts at 91·2—91·7° and is readily soluble in most organic solvents.

Phenyl-6-*chloro*-1-*tolyl*-3-*thiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_6H_3MeCl$, crystallises in glistening needles melting at 132·5—133° and is only sparingly soluble in light petroleum.

6-*Chloro*-3-*acetylaminobenzoic acid*, obtained by the oxidation of the chloroacetotoluidide with permanganate, crystallises from hot water in glistening needles melting at 215—215·5° and is only sparingly soluble in chloroform or benzene. When hydrolysed, it yields 6-chloro-3-aminobenzoic acid, crystallising in colourless needles and melting at 188—188·5°; when heated slightly above its melting point, the acid turns blue. $100\ K = 0 \cdot 0091$. The same acid may be obtained from the

bases described by Goldschmidt and Hönig and by Reverdin and Crépieux and is identical with the acid described by Griess as 2-chloro-3-aminobenzoic acid (Abstr., 1886, 459); 2-chloro-3-toluidine and the isomeric 4-chloro-derivative could not be separated, so the mixture was acetylated.

2-Chloro-3-acetotoluidide crystallises in slender, long needles, melts at 133—134°, and is sparingly soluble in hot water. The same compound may be obtained by the chlorination of *m*-acetotoluidide or by Wynne and Greeves' method. When oxidised, it yields 2-chloro-3-acetylaminobenzoic acid melting at 207—207·5°, and this on hydrolysis yields 2-chloro-3-aminobenzoic acid melting at 160·5—161° (compare Holleman, Abstr., 1902, i, 451).

4-Chloro-3-aminobenzoic acid, obtained by the hydrolysis of the corresponding acetylamino-acid, melts at 216—217 (Greiss gives 212°).

A tabular statement is given of the colours produced when a drop of nitrite solution or of nitric acid is added to various halogen arylamines. J. J. S.

Aromatic Esters of Carbonic and Oxalic Acids. Carl A. Bischoff and August von Hedenström (*Ber.*, 1902, 35, 3431—3437).—Phenyl carbonate, $CO(OPh)_2$, prepared from sodium phenoxide and a solution of carbonyl chloride in toluene, melts at 78° and boils at 167—168° under 15 mm. pressure. *Benzyl carbonate*, $CO(O{\cdot}CH_2Ph)_2$, prepared from the carbonyl chloride and benzyl alcohol, boils at 203·5° under 14 mm. pressure. With benzyl alcohol, phenyl carbonate yields only benzene phenyl ether, but with catechol it yields catechyl carbonate; with resorcinol, it yields *resorcinyl carbonate*, which separates from ethyl oxalate as a white, crystalline powder, sinters at 197°, and melts at 202°; with quinol, it yields *quinol carbonate* melting above 320°; with diphenylethylenediamine and methylaniline it does not interact, but with diphenylamine it yields phenyl diphenylaminocarbonate, $NPh_2{\cdot}CO_2Ph$, and with aniline it yields diphenylcarbamide. T. M. L.

Decomposition of Phenyl Oxalate. Carl A. Bischoff and August von Hedenström (*Ber.*, 1902, 35, 3437—3442).—Phenyl oxalate interacts with diphenylethylenediamine to form diphenyl-2 : 3-diketopiperazine, with di-*o*-tolylethylenediamine to form di-*o*-tolyl-2 : 3-diketopiperazine, with di-α-naphthylethylenediamine to form di-α-naphthyl-2 : 3-diketopiperazine, and with di-β-naphthylethylenediamine to form di-β-naphthyl-2 : 3-diketopiperazine.

Phenyl diphenyloxamate, $NPh_2{\cdot}CO{\cdot}CO_2Ph$, prepared from diphenyloxalate and diphenylamine, crystallises from dilute alcohol in stout, broad, colourless needles and melts at 129°.

Phenyl oxalate interacts with benzyl alcohol to form benzyl oxalate, and with benzhydrol to form the benzhydrol ester, but does not condense with triphenylcarbinol. T. M. L.

Aryl-oxalates. By Carl A. Bischoff and August von Hedenström (*Ber.*, 1902, 35, 3443—3452).—*o-Tolyl oxalate*, $C_2O_2(O{\cdot}C_6H_4Me)_2$, crystallises from alcohol or ether in glistening needles, melts at 91°,

and distils without decomposition. The m-*tolyl* ester crystallises from benzene in glistening needles, melts at 106°, and distils without decomposition. The p-*tolyl* ester forms glistening flakes and melts at 149°. The o-*xylenyl* ester, $C_2O_2(O \cdot C_6H_3Me_2)_2$, crystallises from alcohol in small, glistening, white needles and melts at 106°; the m-*xylenyl* ester melts at 141°, and the p-*xylenyl* ester at 111°.

o-*Xylenyl ethyl oxalate*, $CO_2Et \cdot CO_2 \cdot C_6H_3Me_2$, boils at 161·5°, the m-*xylenyl* ester at 159·5°, and the p-*xylenyl* ester at 156° under 10 mm. pressure.

Carvacryl oxalate, $C_2O_2(O \cdot C_6H_3MePr^{\beta})_2$, crystallises from alcohol in silvery needles and from light petroleum in tablets and melts at 61°. The *thymyl* ester crystallises from alcohol in silvery needles and melts at 61°. *Carvacryl ethyl oxalate* boils at 170° under 10 mm. pressure, and *thymyl ethyl oxalate* at 168° under 10 mm. pressure.

α-*Naphthyl oxalate*, $C_2O_2(O \cdot C_{10}H_7)_2$, crystallises from benzene in colourless needles and melts at 161°. The *β-naphthyl* ester crystallises from acetic acid in colourless, silvery needles and melts at 191°.

Guaiacyl oxalate, $C_2O_2(O \cdot C_6H_4 \cdot OMe)_2$, crystallises from benzene in silvery needles and melts at 127°. The *nitro*-derivative, $C_2O_2[O \cdot C_6H_3(NO_2) \cdot OMe]_2$, separates from nitrobenzene in small, colourless needles and melts at 225—235°.

m-*Nitrophenyl oxalate*, $C_2O_2(O \cdot C_6H_4 \cdot NO_2)_2$, crystallises from xylene in colourless flakes, from ethyl oxalate in needles, is insoluble in the ordinary solvents, and melts at 213°. The p-*nitro* ester crystallises from ethyl oxalate in colourless needles, melts at 257° with slight decomposition, and can also be prepared by nitrating the diphenyl ester. T. M. L.

Oxalates of Divalent Phenols. Diphenyl and Dibenzyl Malonates. CARL A. BISCHOFF and AUGUST VON HEDENSTRÖM (*Ber.*, 1902, **35**, 3452—3457).—*Catechyl oxalate*, $C_2O_4{:}C_6H_4$, crystallises from benzene in needles and melts at 185°. *Resorcinyl oxalate* melts at 260° and is perhaps a polymeric form. *Quinolethyl oxalate*, $OH \cdot C_6H_4 \cdot O \cdot CO \cdot CO_2Et$, crystallises from chloroform in needles, crystallises also from benzene, and melts at 110—111°. *Quinol oxalate*, which like the resorcinyl compound is perhaps a polymeride of the simple substance, melts above 280°.

Phenyl malonate, $CH_2(CO_2Ph)_2$, crystallises from alcohol in colourless needles, melts at 50°, and boils with decomposition at 210° under 15 mm. pressure. *Benzyl malonate* boils at 234·5° under 14 mm. pressure. T. M. L.

Condensation of *tert.*-Butyl Iodide with Resorcinol under the Influence of Ferric Chloride in an Atmosphere of Carbon Dioxide or Oxygen. A. L. GUREWITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 622—625).—When resorcinol (1 mol.), *tert.*-butyl iodide (3 mols.), and a small quantity of sublimed ferric chloride are heated together in a constantly renewed atmosphere of carbon dioxide, a *dibutylresorcinol*, $C_6H_4O_2(C_4H_9)_2$, is formed, which crystallises from dilute alcohol in shining plates melting at 119·5° and is soluble in ether, light petroleum, benzene, chloroform, and carbon disulphide,

Its *diacetyl* derivative, $C_6H_2(C_4H_9)_2(OAc)_2$, separates from dilute alcohol in amorphous crystals which melt at 135° and are soluble in ether, chloroform, benzene, carbon disulphide, light petroleum, or hot acetic acid ; it gives no coloration with ferric chloride solution.

If the reaction is carried out in presence of air, the butyl ether of a dibutylresorcinol (see Abstr., 1899, i, 880) is obtained which, on hydrolysis, yields a *dibutylresorcinol*, which is isomeric with that previously described and melts at 116—118°; it is insoluble in carbon disulphide and forms a *diacetyl* derivative which melts at 137—139° and is soluble in cold acetic acid.

When oxygen is used in place of carbon dioxide, the reaction yields a substance which forms small, white crystals melting at 121° and gives no coloration with ferric chloride ; on hydrolysis with sodium hydroxide solution, it yields a compound forming silvery crystals melting at 117—118° and giving no coloration with ferric chloride.

T. H. P.

Synthesis of Tertiary Alcohols ; Diphenyl Carbinols. HENRI MASSON (*Compt. rend.*, 1902, **135**, 533—534. Compare Abstr., 1901, i, 249).—Tertiary alcohols of the type $R{\cdot}CPh_2{\cdot}OH$ are obtained by the action of magnesium phenyl bromide on the esters of various acids. Ethyl formate, however, yields a secondary alcohol, benzhydrol. The tertiary alcohols thus obtained are usually crystalline; when distilled under the ordinary pressure they yield the corresponding ethylenes, and the latter, when oxidised, yield benzophenone and acids with one carbon atom less than the generating acid, and when treated with alcohol and sodium they yield the corresponding saturated hydrocarbons. In this way, the author has prepared diphenylmethyl carbinol melting at about 81°, which yields diphenylethylene boiling at 270—271° and melting at about 6°, and diphenylethane boiling at 137° under 12 mm. pressure. Diphenylethylcarbinol melts at 91—92° and yields diphenylpropylene which melts at 51° and boils at 280—281°, and diphenylpropane which boils at 142° under 10 mm. pressure. Diphenylpropylcarbinol boils at about 185° under 15 mm. pressure and yields diphenylbutylene boiling at 291—292° and diphenylbutane boiling at 150° under 10 mm. pressure. Diphenylamylcarbinol melts at 46—47°; it yields diphenylhexylene boiling at 314° and diphenylhexane boiling at 164° under 10 mm. pressure. C. H. B.

Synthesis of Aromatic Alcohols. OTTO MANASSE (*Ber.*, 1902, **35**, 3844—3847. Compare Abstr., 1894, i, 577).—*Xylenol-alcohol*, $OH{\cdot}C_6H_2Me_2{\cdot}CH_2{\cdot}OH$ [= 4 : 1 : 3 : 5], prepared by the action of formaldehyde on *m*-xylenol, separates from a mixture of benzene and light petroleum in long needles, melts at 57—58° and gives a blue colour with ferric chloride. *ψ-Cumenol-alcohol*, $OH{\cdot}C_6HMe_3{\cdot}CH_2{\cdot}OH$ [= 5 : 1 : 2 : 4 : 6], from ψ-cumenol and formaldehyde, crystallises from light petroleum in glistening needles and melts at 91—92°. *Eugenol-alcohol*, $OH{\cdot}C_6H_2Pr(OMe){\cdot}CH_2{\cdot}OH$ [= 4 : 1 : 3 : 5], from eugenol and formaldehyde, separates from a mixture of ether and light petroleum in minute needles and melts at 37—38°. *Carvacrol-alcohol*, $OH{\cdot}C_6H_2MePr^{\beta}{\cdot}CH_2{\cdot}OH$, from carvacrol and formaldehyde, crystal-

lises from benzene, and melts at 96—97°. *Hydroxymethyl-o-hydroxyquinoline*, $OH\cdot C_9NH_5\cdot CH_2\cdot OH$, crystallises from a large bulk of warm water and melts at 146—148°. T. M. L.

Pyrogenetic Formation of Anthranilic Acid from *o*-Nitrotoluene. WALTHER LÖB (*Zeit. Elektrochem.*, 1902, 8, 775—777).—A mixture of the vapours of *o*-nitrotoluene and water is brought into contact with a red hot wire (Abstr., 1902, i, 3). Anthranilic acid is formed (about 1·5 grams from 20 grams of *o*-nitrotoluene) together with small quantities of salicylic acid and *o*-cresol and large quantities of resinous acid substances. The material and temperature of the hot wire have but little influence on the result. A *copper* wire, however, reduces part of the material to *o*-toluidine and brings about complete combustion of the remainder; the same result is obtained when *o*-nitrotoluene and steam are passed over red hot copper oxide. T. E.

β-Naphthol Esters of *p*-Acetylamino- and *p*-Benzoylaminobenzoic Acid. FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1902, 35, 3417—3419).—*β-Naphthyl* p-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot C_{10}H_7,$$

is prepared by heating together β-naphthol and *p*-nitrobenzoyl chloride in the presence of dilute aqueous sodium hydroxide; it forms pale yellow needles melting at 166°. *β-Naphthyl* p-*aminobenzoate* is obtained by reducing the nitro-compound with tin and hydrochloric acid; it forms colourless needles melting at 171°; the *platinichloride* is an orange powder, which decomposes without melting. *β-Naphthyl* p-*acetylaminobenzoate*, prepared by boiling the base with acetic anhydride, crystallises in prismatic needles melting at 173°. *β-Naphthyl* p-*benzoylaminobenzoate* separates as a crystalline mass when excess of benzoyl chloride is added to a solution of the base in boiling alcohol; it crystallises in white needles melting at 210°. K. J. P. O.

Transformation of Bromoamides into Amines. ARTHUR HANTZSCH (*Ber.*, 1902, 35, 3579—3580).—The author points out the parallelism between this phenomenon and the Beckmann transformation of oximes. W. A. D.

New Synthesis of Serine. EMIL ERLENMEYER, jun. (*Ber.*, 1902, 35, 3769—3771).—*Ethyl sodium hydroxymethylenehippurate*, $ONa\cdot CH\colon C(NHBz)\cdot CO_2Et$, prepared from ethyl formate and hippurate, is reduced by aluminium amalgam to *ethyl* n-*benzoylserine*,

$$OH\cdot CH_2\cdot CH(NHBz)\cdot CO_2Et,$$

which is hydrolysed to serine and benzoic acid by dilute sulphuric acid. T. M. L.

Action of Carbonyl Chloride and Pyridine on Alcohol Acids. ALFRED EINHORN and CARL METTLER (*Ber.*, 1902, 35, 3639—3643. Compare Abstr., 1898, i, 577).—Benzilide,

$$CPh_2<^{O\cdot CO}_{CO\cdot O}>CPh_2,$$

is obtained by adding carbonyl chloride to a pyridine solution of benzilic acid. *Diphenylglycollide*, $CHPh<\begin{smallmatrix}O\cdot CO\\ CO\cdot O\end{smallmatrix}>CHPh$, results from the action of carbonyl chloride on mandelic acid; it crystallises from acetone in leaflets and melts at 240°.

Tetramethylglycollide, $CMe_2<\begin{smallmatrix}O\cdot CO\\ CO\cdot O\end{smallmatrix}>CMe_2$, produced in a similar manner from hydroxy*iso*butyric acid, is purified by distillation under reduced pressure; it boils at 86° under 11 mm. pressure, melts at 78—79°, and is insoluble in water or sodium carbonate solution.

Phenyl-β-lactic acid and its *o*-nitro-compound, when treated with pyridine and carbonyl chloride, yield cinnamic and *o*-nitrocinnamic acids respectively. G. T. M.

Dicresotides. Alfred Einhorn and Carl Mettler (*Ber.*, 1902, 35, 3644—3646. Compare preceding abstract).—The *dicresotides*, $C_7H_6<\begin{smallmatrix}O\cdot CO\\ CO\cdot O\end{smallmatrix}>C_7H_6$, are prepared by adding carbonyl chloride to a pyridine solution of the cresotic acids.

The *o*-compound crystallises in rectangular plates and melts at 231—231·5°; the *m*- and *p*-derivatives crystallise in needles melting at 207—207·5° and 243° respectively.

These substances, when heated with aniline, give rise to the corresponding anilides, whilst with phenols they yield the aromatic esters of cresotic acids.

The *anilide* of *o*-cresotic acid crystallises in needles and melts at 127°; the corresponding *m*-isomeride melts at 193°.

A small quantity of disalicylide is formed on slowly adding phosphorus oxychloride to a pyridine solution of salicylic acid.

G. T. M.

Action of Carbonyl Chloride and Pyridine on Acid Amides. Alfred Einhorn and Carl Mettler (*Ber.*, 1902, 35, 3647—3653).—Benzonitrile is produced on adding carbonyl chloride to a cold solution of benzamide in pyridine. When salicylamide is employed in this reaction, *o*-hydroxybenzonitrile and *carbonylsalicylamide* are obtained, and these compounds are also formed when the condensation is effected in the presence of aqueous sodium hydroxide solution.

Carbonylsalicylamide, $C_6H_4<\begin{smallmatrix}O—CO\\ CO\cdot NH\end{smallmatrix}$, which is most conveniently prepared by adding ethyl chlorocarbonate to a pyridine solution of salicylamide, is sparingly soluble in the organic solvents and crystallises from glacial acetic acid or the alcohols in needles melting at 227°; its *sodium* derivative, $C_8H_4O_3NNa$, separates from alcohol in white needles; the *silver* derivative, $C_8H_4O_3NAg,H_2O$, crystallises from an ammoniacal solution.

The *benzoyl* derivative, $C_6H_4<\begin{smallmatrix}O—CO\\ CO\cdot NBz\end{smallmatrix}$, produced by adding benzoyl chloride to a pyridine solution of carbonylsalicylamide, crystallises

from alcohol in needles melting at 172°. The *methyl* derivative,

$$C_6H_4<\begin{matrix}O-CO\\ CO\cdot NMe\end{matrix},$$

results from the action of methyl iodide on the sodium derivative, and crystallises from methyl alcohol in needles melting at 146°; the *ethyl* derivative, prepared in a similar manner, melts at 107°.

The *phenacyl* derivative, $C_6H_4<\begin{matrix}O-CO\\ CO\cdot N\cdot CH_2\cdot COPh\end{matrix}$, prepared by adding bromoacetophenone to the sodium derivative suspended in absolute alcohol, crystallises from acetone in needles melting at 187°.

Carbonylsalicylchloroamide, $C_6H_4<\begin{matrix}O-CO\\ CO\cdot NCl\end{matrix}$, produced by passing chlorine into a cold aqueous solution of the sodium derivative, is a sparingly soluble substance, separating from glacial acetic acid as a white precipitate melting at 179—180°. When heated with aniline, carbonylsalicylamide is decomposed, yielding diphenylcarbamide and salicylamide.

Carbonyl m-*methylsalicylamide*, $\begin{matrix}CH:CH\cdot CO-CO\\ CMe:CH\cdot C\cdot CO\cdot NH\end{matrix}$, prepared by adding ethyl chlorocarbonate to a pyridine solution of *m*-methylsalicylamide, crystallises from alcohol in needles melting at 233°. Neither this substance nor its lower homologue gives a coloration with ferric chloride. G. T. M.

Study of Carbonylsalicylamide. ALFRED EINHORN and JULIUS SCHMIDLIN (*Ber.*, 1902, **35**, 3653—3656. Compare preceding abstract).—Carbonylsalicylamide may be produced from salicylamide by heating this substance with amyl chlorocarbonate, phenyl carbonate, or phenylcarbimide. When the aromatic amide is heated at 250° with carbamide, carbonylsalicylamide is also obtained mixed with tri-*o*-hydroxyphenyltriazine (trihydroxycyaphenine),

$$C_3N_3(C_6H_4\cdot OH)_3.$$

Salicylic acid and carbamide also furnish a certain amount of carbonylsalicylamide. G. T. M.

Action of Mixed Organo-magnesium Compounds on Ketonic Esters. II. VICTOR GRIGNARD (*Compt. rend.*, 1902, **135**, 627—630. Compare Abstr., 1902, i, 420).—It has been shown that β-ketonic esters give anomalous reactions with organo-magnesium compounds, but it has now been found that the other ketonic esters react quite normally. The carbonyl group enters into reaction before the carboxyl group, and in the synthesis of acid-alcohols excess of the organo-magnesium compound must be avoided. With methyl magnesium iodide, ethyl pyruvate gives iso*amyl* α-*hydroxy*iso*butyrate* as a colourless liquid with a pleasant odour, which boils at 195—198°, has a sp. gr. 0·9405 at 17·8°/4°, and n_D 1·4233. With *iso*amyl magnesium bromide, the same ester gives *methyl*iso*amylglycollic acid*, which crystallises in fine needles and melts at 72—73°. With α-naphthyl magnesium bromide, the pyruvic ester yields α *naphthylmethylglycollic acid*, which crystallises from 50 per cent. alcohol with $\frac{1}{2}H_2O$, and melts at 143°.

Methyl magnesium iodide gives *ethyl phenylmethylglycollate* when treated with ethyl phenylglyoxalate; it is a pale yellow liquid which boils at 258—260°, has a sp. gr. 1·100 at 11°/4°, and n_D 1·50997. By saponification, the free *phenylmethylglycollic acid* is obtained which crystallises with $\frac{1}{2}H_2O$ and melts at 67—68°. The same ester gives with ethyl magnesium bromide *ethyl phenylethylglycollate* as a pale yellow liquid which boils at 142—145° under 18 mm. pressure. The corresponding acid crystallises without water and melts at 126°.

Ethyl lævulate, with ethyl magnesium bromide, gives the lactone $CH_2<\begin{matrix}CMeEt-\\CH_2\cdot CO\end{matrix}>O$ as a colourless, mobile liquid which boils at 105—106° at a pressure of 18 mm.; it has a sp. gr. 1·0085 at 13·7°/4° and n_D 1·44320. The glycol, $OH\cdot CMeEt\cdot CH_2\cdot CH_2\cdot CEt_2\cdot OH$, boils at 138—140° under 14 mm. pressure and crystallises from benzene in needles which melt at 61°. With *iso*amyl magnesium bromide, the lactone $CH_2<\begin{matrix}CMe(C_5H_{11})\\CH_2\text{——}CO\end{matrix}>O$ is obtained as a colourless liquid which boils at 133—134° under 15 mm. pressure, has a sp. gr. 0·9566 at 15·9°/4° and n_D 1·44964. The glycol

$$C_5H_{11}\cdot CMe(OH)\cdot C_2H_4\cdot C(C_5H_{11})_2\cdot OH$$

is a viscous liquid which boils at 205—208° under 15 mm. pressure. With phenyl magnesium bromide, the lactone $CH_2<\begin{matrix}CMePh-\\CH_2\cdot CO\end{matrix}>O$ is formed; it is a yellowish liquid, which boils at 168—170° under 16 mm. pressure and has a sp. gr. of 1·1173 at 17·4°/4° and n_D 1·52996. At the same time, the oxide of the corresponding glycol is formed, $\begin{matrix}CH_2\cdot CMePh\\ | \\ CH_2\text{——}CPh_2\end{matrix}>O$, which is a viscous liquid boiling at 245—250° under 17 mm. pressure.

The reaction with methyl magnesium iodide and ethyl acetylsuccinate does not proceed as in the case of the other γ-ketonic esters, but it appears to react in the enolic form. A small quantity of terebic acid can, however, be obtained from the reaction product.

J. McC.

α-Hydroxyphenylbutyrolactone and its Conversion into Benzoylpropionic Acid. EMIL ERLENMEYER, jun. (*Ber.*, 1902, 35, 3767—3769).—*α-Hydroxyphenylbutyrolactone*,

$$CHPh<\begin{matrix}CH_2\cdot CH\cdot OH\\ \quad\ \ | \\ O\text{——}CO\end{matrix},$$

prepared by reducing benzoylpyruvic acid with sodium amalgam, separates from chloroform or light petroleum in colourless crystals, melts at 125°, and is converted by heating for two hours with dilute hydrochloric acid into β-benzoylpropionic acid. T. M. L.

Halogen-substituted Derivatives of Indoxyl. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 131401).—A *bromoindoxyl* is readily obtained by treating indoxyl or indoxylic acid dissolved in dilute hydrochloric acid with bromine water; it yields a bromoindigotin either when heated with hydrochloric acid or sodium acetate or when

oxidised in the presence of alkaline compounds. This bromination can also be effected in the presence of finely divided magnesia. The chlorination is carried out by adding a solution of calcium hypochlorite to one containing the indoxyl dissolved in dilute acetic acid.

G. T. M.

Synthesis of Indigo-blue from *o*-Nitroacetophenone. RUDOLF CAMPS (*Arch. Pharm.*, 1902, 240, 423—437).—The oil obtained as a bye-product in the reduction of *o*-nitroacetophenone to *o*-amino-acetophenone (Abstr., 1900, i, 115) can be obtained in comparatively large quantity by regulating the reduction, the acid used being weak and in limited amount, or a neutral reducing agent being employed. It is formed whether the reducing agent is tin and hydrochloric acid, stannous chloride and hydrochloric acid, zinc dust and water, or amalgamated aluminium and water. It is also formed when *o*-nitro-acetophenone is pounded with ten times its weight of a mixture of soda lime with zinc dust (2 : 13); the reaction often begins spontaneously, and can be induced in any case by gentle warming; it is completed by warming for a time at 30—40°. This oil was undoubtedly an intermediate product in Emmerling and Engler's synthesis of indigo from *o*-nitroacetophenone (*Ber.*, 1870, 3, 885; Abstr., 1895, i, 231).

The oil boils at 121—122° under 17 mm. pressure and appears to be *di-o-acetylhydrazobenzene*, $N_2H_2(C_6H_4 \cdot COMe)_2$; it has feebly basic properties, forms a *platinichloride*, $C_{16}H_{16}O_2N_2,H_2PtCl_6,2H_2O$, yields indigotin when heated, even when air is excluded, and when treated in cooled hydrochloric acid solution with sodium nitrite, forms a *substance* melting at 101—102°, probably di-*o*-acetylazoxybenzene or perhaps *o*-nitrosoacetophenone, which yields indigotin when it is heated with water.

C. F. B.

Preparation of Indigotin from *a*-Thioisatin. J. R. GEIGY & Co. (D.R.-P. 131934).—*a-Thioisatin*,

$$C_6H_4{<}{}^{N}_{CO}{>}C\cdot SH \quad \text{or} \quad C_6H_4{<}{}^{NH}_{CO}{>}C:S,$$

is produced by adding simultaneously to cold water an aqueous solution of sodium hydrosulphide and a concentrated sulphuric acid solution of *a*-isatinanilide; it separates in the form of a voluminous paste which, when treated with a solution of alkali hydroxide, hydrosulphide, or carbonate in the presence of hydrogen sulphide, yields indigotin in a finely divided condition.

G. T. M.

Reduction of Indigotin with Zinc Dust and Ammonia. A. KUFFERATH (*Zeit. Farb. Text. Chem.*, 1902, 1, 481).—Two indigo vats were prepared with artificial indigotin, zinc dust, and ammonia, one being maintained at 0° and the other at 80°. The clear solution from the cold vat gave the larger precipitate on oxidation, but the percentage of indigotin in the precipitated pigment obtained from the cold vat was only 50 while that from the warm vat was 78·37. A greater amount of indigo-white exists in an insoluble form in the warm vat, the precipitation of this slightly acid compound being due

to the hydrolytic dissociation of its ammonium derivative in the warm solution. A large excess of ammonia (17 mols.) is required to keep indigo-white in solution, even at the ordinary temperature. G. T. M.

Ionic Phenomena Exhibited by Colouring Matters. ARTHUR G. GREEN (*Zeit. Farb. Text. Chem.*, 1902, i, 413—414).—When a cold aqueous solution of phenolphthalein has been almost decolorised by the addition of excess of sodium hydroxide, it may be partially neutralised with acetic acid without developing any coloration, and even when the solution is acidified with the same acid and again rendered alkaline, it does not acquire the deep red colour due to the ordinary alkali salt. On the other hand, the colourless acid or neutral solution, when previously boiled, becomes turbid on cooling, and then gives the normal red coloration. These phenomena are most readily explained in terms of the quinone hypothesis. The red quinonoid sodium salt. $CO_2Na{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OH){:}C_6H_4{:}O$, when treated with excess of the alkali, passes into the colourless triphenylcarbinol derivative, $CO_2Na{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OH)_2{\cdot}OH$, which, when neutralised, yields the corresponding carbinol-acid, $CO_2H{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OH)_2{\cdot}OH$, and this substance, on boiling, undergoes internal dehydration, yielding the colourless lactone, $\begin{matrix}CO{\cdot}O\\ | \\ C_6H_4\end{matrix}\!\!>\!C(C_6H_4{\cdot}OH)_2$. This lactone, when treated with one mol. of sodium hydroxide, furnishes the red quinonoid salt.

Magenta, crystal-violet, and malachite-green, when dissolved in excess of hydrochloric acid, yield orange-yellow solutions which retain their colour when treated with sodium chloride solution, but develop the characteristic colorations of the colouring matters when diluted with water. The diluted solutions again assume the yellow colour when saturated with sodium chloride or some other metallic chloride. Sodium acetate, on the other hand, causes the yellow solutions to develop the characteristic colorations of the dyes.

The yellow solutions probably contain yellow carbonium chlorides, analogous to triphenylmethyl chloride (Abstr., 1902, i, 534, 600), and these salts undergo hydrolytic dissociation when their solutions are diluted, yielding the corresponding carbinols; these intermediate products immediately lose water, and pass over into the quinonoid anhydrides which possess the characteristic colours of the colouring matter. The addition of metallic chlorides leads to the production of double salts, and these products, being more stable than the carbonium chlorides themselves, are less dissociated by water. G. T. M.

Haloid and Nitro-derivatives of Naphthalic Anhydride. Influence of the Substituents on Fluorescence. LUIGI FRANCESCONI and G. BARGELLINI (*Gazzetta*, 1902, 32, ii, 73—96).—The authors give a short account of the theory of fluorescence put forward by Meyer (Abstr., 1898, ii, 105, 275), according to which fluorescence of a substance is held to be due to the presence in the molecule of one of a number of definite atomic groupings. The blue fluorescence given by naphthalic anhydride with concentrated sulphuric acid is readily explainable, since this anhydride contains one of the

so-called fluorophore groupings, namely, the pyrone ring. They adversely criticise Hewitt's theory (Proc., 1900, 16, 3).

The method in which the fluorophore ring is combined with benzene nuclei in any compound is without influence on the fluorescence, as is also the manner in which the separate atoms in the fluorophore ring itself are united.

In order to see how the fluorescence exhibited by naphthalic anhydride with concentrated sulphuric acid is affected by the introduction of substituents into the molecule of the anhydride, and hence, also, to test Meyer's rules with regard to the influence of substituents, the authors have prepared and examined a number of haloid and nitro-derivatives of this compound. The results obtained are briefly as follows. The entrance of chlorine into the molecule changes the colour of the fluorescence to green, whilst the intensity diminishes continuously as the number of substituent chlorine atoms increases, until finally hexachloronaphthalic anhydride exhibits no fluorescence. The introduction of a bromine atom diminishes the fluorescence, which, however, retains its blue colour, whilst the presence of an iodine atom or a nitro-group in the molecule of naphthalic anhydride causes the entire loss of fluorescence. As regards the extent to which these four substituents act in decreasing the fluorescing power of the anhydride, they stand in the order: nitro-group, iodine, bromine, chlorine.

Juvalta's method (D.R.-P. 50177), in which the anhydride is treated in fuming sulphuric acid solution with the halogen, was employed for the preparation of the haloid derivatives of naphthalic anhydride. The results obtained by this method were found to vary widely with but slight changes in the conditions of the reaction, such as the temperature and time, the proportion of sulphur trioxide in the sulphuric acid, and the amount of halogen employed.

By passing chlorine into a solution of naphthalic anhydride in a mixture of equal weights of fuming and ordinary concentrated sulphuric acid containing a small quantity of iodine and gradually heating the liquid up to 180—200°, tetrachloro- and a small proportion of trichloro-naphthalic anhydride were obtained.

Trichloronaphthalic anhydride, $C_{10}H_3Cl_3<^{CO}_{CO}>O$, crystallises from benzene in mammillary aggregates of needles and from acetic acid in small, iridescent needles, which melt at 183—185° and are soluble in nitrobenzene, concentrated nitric acid, or ethyl acetate, and to a slight extent in alcohol, light petroleum, or ether. Hot potassium hydroxide solution dissolves it and, on cooling, deposits the potassium salt in the form of white needles.

Tetrachloronaphthalic anhydride, $C_{10}H_2Cl_4<^{CO}_{CO}>O$, crystallises from benzene solution in large, white prisms melting at 235—236°, and is soluble in ethyl acetate and slightly so in acetic acid, concentrated nitric acid, or nitrobenzene. It dissolves in hot potassium hydroxide solution, which, when cold, deposits the potassium salt as a white, crystalline powder. The corresponding *tetrachloronaphthal-*

imide, $C_{10}H_2Cl_4<\begin{matrix}CO\\CO\end{matrix}>NH$, crystallises from acetic acid in pale yellow, slender needles, which melt at 302—303° and sublime in rhombic plates; it is readily soluble in nitrobenzene. The *oxime*, $C_{10}H_2Cl_4<\begin{matrix}\text{—CO—}\\C(:NOH)\end{matrix}>O$, is deposited from acetic acid solution in golden-yellow, slender needles, which melt at 263—264° and dissolve in nitrobenzene; with sodium carbonate, it yields a *sodium* salt of a wine-red colour slightly soluble in water. The *phenylhydrazone*, $C_{18}H_8O_2N_2Cl_4$, which is formed in the cold, crystallises from benzene in long, woolly, yellow needles melting at 269—270° and soluble in nitrobenzene. When tetrachloronaphthalic anhydride and phenylhydrazine are heated together on a water-bath, a *compound* is obtained which separates from nitrobenzene solution in small, orange-coloured crystals melting at 237—238°; its formula was not determined.

Hexachloronaphthalimide, $C_{10}Cl_6<\begin{matrix}CO\\CO\end{matrix}>NH$, is deposited from acetic acid as an intensely yellow, crystalline powder, which melts at 260—261° and is soluble in alcohol; it is dissolved by concentrated sulphuric acid, yielding a yellow, non-fluorescent solution.

By heating a solution of naphthalic anhydride in a mixture of fuming and concentrated sulphuric acids, to which bromine is gradually added, three products are obtained: (1) a non-halogenated acid containing sulphur and melting at about 240°, (2) a substance melting at about 160°, and (3) bromonaphthalic anhydride, identical with the compound obtained by Blumenthal (*Ber.*, 1874, 7, 1092). This substance gives a blue fluorescence with concentrated sulphuric acid, but as it is difficult to purify, the phenomenon may be due to slight admixture of naphthalic anhydride. From the solutions of bromonaphthalic anhydride in aqueous alkali hydroxide, hydrochloric acid precipitates the corresponding acid in white flocks. *Bromonaphthalimide*, $C_{10}H_5Br<\begin{matrix}CO\\CO\end{matrix}>NH$, crystallises from acetic acid in white needles melting at 284° and dissolving to a slight extent in benzene or alcohol; it gives a yellow coloration but no fluorescence with sulphuric acid. The *oxime* of bromonaphthalic anhydride, $C_{10}H_5Br<\begin{matrix}\text{—CO—}\\C(:NOH)\end{matrix}>O$, separates from acetic acid solution in pale yellow needles which melt at 278—280° and dissolve slightly in alcohol, benzene, or ethyl acetate; it forms a red, slightly soluble sodium derivative. The *phenylhydrazone*, $C_{18}H_{11}O_2N_2Br$, crystallises from alcohol in silky, pale yellow needles melting at 222—223°; it is soluble in benzene or acetic acid.

The action of iodine on naphthalic anhydride in sulphuric acid solution yields:

(1) *Iodonaphthalic acid*, $C_{10}H_5I(CO_2H)_2$, which is soluble in all the ordinary organic solvents and melts at about 217°, but could not be completely freed from a substance crystallising in silky, white needles.

(2) *Tri-iodonaphthalic anhydride*, $C_{10}H_3I_3{<}^{CO}_{CO}{>}O$, crystallises from nitrobenzene in yellow needles melting at 256—257° and is slightly soluble in alcohol or acetic acid; it dissolves in concentrated sulphuric acid, giving a pale yellow coloration but no fluorescence. The corresponding *imide*, $C_{12}H_4O_2NI_3$, separates from nitrobenzene in pale yellow needles which begin to lose iodine, but do not melt at 325°; sulphuric acid dissolves it, giving a yellow coloration but no fluorescence. The *oxime*, $C_{12}H_4O_3NI_3$, crystallises from nitrobenzene in yellow needles which begin to lose iodine at 310° and decompose completely without melting at 320°; it is slightly soluble in acetic acid and forms a yellowish-red sodium salt. The *phenylhydrazone*, $C_{18}H_9O_2N_2I_3$, is deposited from solution in nitrobenzene in pale yellow crystals which melt and decompose at 305—310°. If the tri-iodonaphthalic anhydride and phenylhydrazine be heated at 170° instead of 100°, ammonia is evolved and (1) a red compound melting at about 100° and very soluble in ether or benzene, and (2) a dark yellow compound melting at about 200° are formed but were not further investigated. *Tri-iodonaphthalic acid*, $C_{10}H_3I_3(CO_2H)_2$, forms a white, flocculent precipitate; its silver salt forms a reddish-white precipitate which gradually turns violet.

Dinitronaphthalic acid, $C_{10}H_4(NO_2)_2(CO_2H)_2$, obtained by the action of fuming nitric acid on a solution of naphthalic anhydride in concentrated sulphuric acid, crystallises from water in silvery-white leaflets which melt at 208—210° and are soluble in acetic acid, alcohol, ethyl acetate, nitrobenzene, or amyl alcohol; it dissolves readily in concentrated nitric acid and the solution deposits a yellowish-white substance melting and decomposing at 266°; this is soluble in concentrated sulphuric acid, giving a colourless solution which exhibits no fluorescence.

The fluoresceins of the substituted naphthalic anhydrides were prepared by heating with resorcinol in presence of zinc chloride and were examined in alkaline solutions with regard to their colour and fluorescence, the results being given in the following table:

Fluorescein.	Colour.	Fluorescence.
From naphthalic anhydride	Dark orange	Very intense green
,, trichloronaphthalic anhydride......	Pale orange	Intense green
,, tetrachloronaphthalic anhydride...	Darker orange	Less intense green
,, hexachloronaphthalic anhydride...	Brownish-red	Slight green
,, bromonaphthalic anhydride.........	Pale orange	Very intense green
,, tri-iodonaphthalic anhydride	Cherry-red	Faint green
,, iodonaphthalic acid	Pale orange	Intense green
,, dinitronaphthalic acid	Brownish-red	Very faint green

The alkaline solutions of all these fluoresceins dye silk different shades of red according to the dilution of the bath and the duration of immersion. The most vivid tints are obtained with the fluoresceins from tetrachloro- and tri-iodo-naphthalic anhydrides. T. H. P.

p-Dimethylaminobenzaldehyde. FRANZ SACHS and WILLY LEWIN (*Ber.*, 1902, **35**, 3569—3578).—p-*Dimethylaminobenzaldehydecyanohydrin*, $NMe_2·C_6H_4·CH(OH)·CN$, prepared by the interaction of

the aldehyde with anhydrous hydrogen cyanide at 0°, is precipitated from its chloroform solution by light petroleum as a white, flocculent mass melting at 113—114°; by concentrated sulphuric acid at the ordinary temperature, it is converted into p-*dimethylaminomandelamide*, $NMe_2\cdot C_6H_4\cdot CH(OH)\cdot CO\cdot NH_2$, which separates from hot water in small crystals and melts at 195°; *barium* p-*dimethylaminomandelate*, $C_{20}H_{24}O_6N_2Ba$, forms white needles and is sparingly soluble in water. *a-Cyano*-p-*dimethylaminobenzylaniline*, $NMe_2\cdot C_6H_4\cdot CH(CN)\cdot NHPh$, obtained by heating the cyanohydrin with aniline for 2 hours at 60°, forms white, rhombohedral crystals, melts at 114°, and is oxidised by potassium permanganate in acetone solution to *4'-dimethylaminophenylphenyl-μ-cyanoazomethine*, $NMe_2\cdot C_6H_4\cdot C(CN)\colon NPh$, which crystallises from light petroleum in orange-yellow prisms and melts at 121°. p-*Dimethylaminobenzylideneaniline*, $NMe_2\cdot C_6H_4\cdot CH\colon NPh$, obtained by heating the components on the water-bath, forms greenish-yellow crystals melting at 100°.

The following derivatives were prepared similarly from *p*-toluidine: *a-Cyano*-p-*dimethylaminobenzyl*-p-*toluidine*, white crystals, melting at 127—128°; *4'-dimethylaminophenyl-4-tolyl-μ-cyanoazomethine*, yellow needles, melting at 154—155°; p-*dimethylaminobenzylidene*-p-*toluidine*, slender, bright yellow needles, melting at 120—121°. From *o*-anisidine and *p*-anisidine, *a-cyano*-p-*dimethylaminobenzylanisidines* melting at 133° and 109—110°; *4'-dimethylaminophenylmethoxyphenyl-μ-cyanoazomethines* melting at 148—149° and 133—134°; and p-*dimethylaminobenzylideneanisidines* melting at 113—114° and 138—140° respectively, were obtained. *a-Cyano*-p-*dimethylaminobenzyl*-p-*phenetidine* melts at 100°; *4'-dimethylaminophenyl-4-ethoxyphenyl-μ-cyanoazomethine* at 133—134°, and p-*dimethylaminobenzylidine*-p-*phenetidine* at 145—146°.

p-Dimethylaminobenzaldehydecyanohydrin condenses much more slowly with methylaniline than with the primary bases; *a-cyano*-p-*dimethylaminobenzylmethylaniline*, $NMe_2\cdot C_6H_4\cdot CH(CN)\cdot NMePh$, is only obtained on heating the components for 3 hours at 120° along with a little alcohol, and crystallises from light petroleum in white needles melting at 102—103°; the corresponding *amide*,

$$NMe_2\cdot C_6H_4\cdot CH(CO\cdot NH_2)\cdot NMePh,$$

is easily soluble in alcohol, sparingly so in water, and melts at 170°.

p-*Dimethylaminobenzylideneacetone*, $NMe_2\cdot C_6H_4\cdot CH\colon CH\cdot COMe$, is readily obtained by adding a few drops of aqueous sodium hydroxide to an alcoholic solution of *p*-dimethylaminobenzaldehyde and acetone (1 mol.); it separates from alcohol in orange-yellow, spear-shaped crystals, sinters at 230°, melts at 234—235°, and condenses with *p*-dimethylaminobenzaldehyde (1 mol.) in alkaline alcoholic solution to form *tetramethyl*-p-*diaminodibenzylideneacetone*,

$$CO(CH\colon CH\cdot C_6H_4\cdot NMe_2)_2.$$

This crystallises from alcohol in dark yellow or orange-coloured leaflets, melts at 191°, and gives a *picrate* melting at 163—165°.

p-*Dimethylaminobenzylideneacetophenone*, $NMe_2\cdot C_6H_4\cdot CH\colon CH\cdot COPh$, obtained from *p*-dimethylaminobenzaldehyde and acetophenone, separates from alcohol in yellow crystals and melts at 114°, the *picrate* melts at 150°.

m-Nitro-p-*dimethylaminobenzaldehyde* cannot be obtained by

Knöller and Nossek's method (*Ber.*, 1887, 20, 3194), but is prepared by adding *p*-dimethylaminobenzaldehyde to an excess of cold nitric acid free from nitrous fumes; it melts at 103—105° and yields with acetophenone (1 mol.) the *compound*, $NMe_2\cdot C_6H_3(NO_2)\cdot CH{:}CH\cdot COPh$, melting at 130—131°.

p-*Dimethylaminobenzylidenemalononitrile*, $NMe_2\cdot C_6H_4\cdot CH{:}C(CN)_2$, prepared by the interaction of the components at the ordinary temperature in presence of piperidine, crystallises from absolute alcohol in long, red needles, and melts at 179—180°.

p-*Dimethylaminobenzylidene*-p-*nitrobenzyl cyanide*,

$$NMe_2\cdot C_6H_4\cdot CH{:}C(CN)\cdot C_6H_4\cdot NO_2,$$

crystallises from glacial acetic acid in dark purple-red needles melting at 245°.

p-*Dimethylaminobenzylidenebarbituric acid*,

$$NMe_2\cdot C_6H_4\cdot CH{:}C{<}{}^{CO\cdot NH}_{CO\cdot NH}{>}CO,H_2O,$$

obtained by heating the components for three-quarters of an hour at 145—150°, separates from glacial acetic acid in scarlet-red crystals and melts and decomposes at 268°.

It is pointed out that whereas the compound

$$C_6H_5\cdot C(CN){:}N\cdot C_6H_4\cdot NMe_2,$$

is orange-red, the compound, $NMe_2\cdot C_6H_4\cdot C(CN){:}NPh$, is much lighter coloured (orange-yellow), whilst the unsubstituted form,

$$C_6H_5\cdot C(CN){:}NPh,$$

is lemon-yellow. The cyano-group, moreover, is auxochromic, since, for example, $NMe_2\cdot C_6H_4\cdot C(CN){:}NPh$ is much more coloured than $NMe_2\cdot C_6H_4\cdot CH{:}NPh$. W. A. D.

Chemical Action of Light. IV. GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Atti R. Accad. Lincei*, 1902, [v], 11, ii, 145—151; *Ber.*, 1902, 35, 3593—3598. Compare Abstr., 1901, i, 390, 547; 1902, i, 433).—In order to determine which rays of the spectrum cause the accelerating action in the reactions previously studied by them (*loc. cit.*), the authors have investigated the actions of two kinds of light; (1) a red light, obtained by absorption with an alcoholic solution of fluorescein and gentian-violet, and (2) a bluish-violet light for which a 10 per cent. alcoholic solution of cobalt chloride was employed, on the various reactions given below. Glass tubes containing the reacting substances were immersed in these solutions contained in glass cylinders, which were then exposed to the action of sunlight.

An ethereal solution of quinone remains unchanged in red light, whilst in blue light long, black needles of quinhydrone begin to separate after six hours. In red light, an alcoholic solution of quinone becomes slightly brown, whilst in blue light the darkening is much greater and quinol, quinhydrone, acetaldehyde, and a black, amorphous substance are formed. In red light, an aqueous solution of glycerol and quinone undergoes a slight darkening in colour, but the quinone can be almost entirely recovered, whilst in blue light the quinone is partially transformed into a blackish mass.

An alcoholic solution of benzophenone remains unchanged in red light whilst in blue light it yields benzopinacone.

A solution of benzil in alcohol is turned faintly green by red light, but in blue light it deposits crystals of benzylbenzoin.

In red light, an alcoholic vanillin solution remains unchanged, whilst with blue light it yields dehydrovanillin.

A benzene solution of *o*-nitrobenzaldehyde is unaltered by red light, but is converted by yellowish-green, or more quickly by blue, light into *o*-nitrosobenzoic acid. In blue light, an alcoholic *o*-nitrobenzaldehyde solution yields *o*-nitrobenzoic acid and its ethyl ester. The transformation, observed by Friswell (Proc., 1897, **13**, 148), of nitrobenzene into a black mass by sulphuric acid, only takes place in blue and not in red light; the author has been unable to determine the nature of the compound produced.

In red light, a paraldehyde solution of *o*-nitrosobenzoic acid remains unchanged, whilst under the influence of blue light it yields the compound $C_9H_7O_3N$, previously obtained by the authors (Abstr., 1902, i, 378).

In all these cases it is seen that the reactions are favoured by the more refrangible rays. The accelerating influence is hence a photochemical one and is not due to the prolonged action of solar heat.

T. H. P.

Theory of the Action of Ferric Chloride in the Synthesis of Organic Compounds. A. L. GUREWITSCH (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 625—629).—From a consideration of the different syntheses of organic compounds by the agency of ferric chloride, the author draws conclusions as to the mechanism of the reaction. The various steps in the formation of keto-phenols from phenols and acid chlorides are probably as follows: (1) $C_6H_4(OH)_2 + 2FeCl_3 = C_6H_4(O)_2 2FeCl_2 + 2HCl$; (2) $2RCOCl + 2FeCl_3 = (RCOCl)_2 2FeCl_3$; (3) $C_6H_4O_2 2FeCl_2 + (RCOCl)_2 2FeCl_3 = C_6H_4(OCOR)_2 4FeCl_3$;

(4) $C_6H_4(OCOR)_2 4FeCl_3 = C_6H_2(OH)_2(RCO)_2 + 4FeCl_3$.

When an anhydride is used in place of the acid chloride, the latter is most probably formed from the former according to the equation: $6Ac_2O + 2FeCl_3 = 2Fe(OAc)_3 + 6AcCl$; the other steps in the synthesis of the keto-phenol are then the same as those represented in the four equations given above.

T. H. P.

Condensation of Phenoxyacetone with Benzaldehyde. RICHARD STOERMER and R. WEHLN (*Ber.*, 1902, **35**, 3549—3560).—*Benzylidenephenoxyacetone*, CHPh:C(OPh)·COMe, obtained when equal molecules of benzaldehyde and phenoxyacetone are condensed either in the presence of sodium hydroxide or hydrogen chloride, forms colourless crystals, melts at 102°, and when oxidised with sodium hypochlorite yields phenoxycinnamic acid; the *oxime* crystallises in pale yellow needles melting at 169°, the *phenylhydrazone* in yellowish leaflets melting at 118°, and the *semicarbazone* in lustrous, white needles melting at 216°. p-*Methoxybenzylidenephenoxyacetone* crystallises from alcohol in bright yellow leaflets and melts at 106° and yields α-phenoxy-*p*-methoxycinnamic acid when oxidised; its *oxime*

crystallises in lustrous, white needles which melt at 179°, the *phenylhydrazone* in golden leaflets which melt at 101°, and the *semicarbazone* in lustrous, feathery needles which melt at 193°. o-*Hydroxybenzylidenephenoxyacetone* crystallises from dilute alcohol in pale yellow plates with diagonal striæ, melts at 153°, and, when oxidised with sodium hypochlorite, yields α-phenoxy-*o*-coumaric acid; it yields a *semicarbazone*, which separates from alcohol in lustrous, feathery crystals and melts at 220°.

Phenoxyacetone condenses with two mols. of benzaldehyde, forming *dibenzylidenephenoxyacetone*, CHPh:C(OPh)·CO·CH:CHPh, which crystallises from alcohol in bright yellow leaflets and melts at 154°; the analogous *compound* from anisaldehyde is yellow and melts at 136°. The *compound*, CHPh:C(OPh)·CO·CH:CH·C_6H_4·OMe, obtained by the successive condensation of phenoxyacetone with benzaldehyde and anisaldehyde, forms yellow crystals and melts at 119—120°; the analogous *compound*, OMe·C_6H_4·CH:C(OPh)·CO·CH:CHPh, crystallises in yellow needles and melts at 155°.

Benzylphenoxyacetone, CH_2Ph·C(OPh)·COMe, obtained by the reduction of the corresponding benzylidene compound, is a viscous oil, which boils at 180—183° under 14 mm. pressure. When oxidised with sodium hypochlorite, it yields phenoxyphenylpropionic acid, and condenses with benzaldehyde, forming a *compound* melting at 95°; when treated with cold concentrated sulphuric acid, it yields a *compound*, $C_{16}H_{14}O$, which forms hard crystals melting at 29°, boils at 198—200° under 15 mm. pressure, and is probably benzylmethylcoumarone.

The constitution of the condensation products of benzaldehyde with unsymmetrical ketones, R·CH_2·CO·CH_2R^1, is in general readily proved by oxidation with sodium hypochlorite; thus, for example, when oxidised, the compound CHPh:CMe·COMe (Harries and Müller, Abstr., 1902, i, 296) yields α-methylcinnamic acid. R. H. P.

Action of Phenoxyacetyl Chloride on Benzene and its Derivatives. Richard Stoermer and P. Atenstädt (*Ber.*, 1902, 35, 3560—3565).—When phenoxyacetyl chloride reacts with benzene in the presence of aluminium chloride, a 15 per cent. yield of coumaranone is obtained in addition to phenoxyacetophenone as described by Vandevelde (Abstr., 1900, i, 30). Coumaranone condenses with *o*-nitrobenzaldehyde in the presence of hydrochloric acid, forming o-*nitrobenzylidenecoumaranone*, $C_{15}H_9O_4N$, which crystallises in orange-yellow, slender, felted needles, and melts at 195—196°. Attempts to convert phenoxyacetophenone into phenylcoumarone were unsuccessful; it, however, yields a *sulphonic acid*, $C_{14}H_{12}O_5S$, which crystallises from hot water, melts at 165°, and forms crystalline *barium* (with $4H_2O$) and *sodium* (with $2H_2O$) salts.

Analogous condensations of phenoxyacetyl chloride with homologues of benzene gave similar results, but with an increasing yield of ketone and decreasing yield of the coumaranones. p-*Tolyl phenoxymethyl ketone* crystallises in white needles, melts at 73°, boils at 210—215° under 12 mm. pressure, and forms an *oxime* melting at 96° and a *sulphonic acid* melting at 167°. m-*Xylyl phenoxymethyl ketone* crystallises in long, white needles, melts at 65°, boils at 256—258° under

60 mm. pressure, and forms an *oxime*, which crystallises in clusters of white needles melting at 122—123°, and a *sulphonic acid* melting at 138°. *Anisyl phenoxymethyl ketone* melts at 67° and boils at 230—233° under 20 mm. pressure; the *oxime* crystallises in white needles and melts at 105°. p-*Ethoxyphenyl phenoxymethyl ketone* crystallises in white needles melting at 102°, boils at 245—248° under 25 mm. pressure, and its *oxime* crystallises in needles and melts at 116°. 1 : 3-*Dimethoxyphenyl phenoxymethyl ketone* melts at 118·5° and boils at 260—264° under 18 mm. pressure. α-*Phenoxypropionyl chloride* is a colourless liquid with an unpleasant odour, and boils at 115—117° under 10 mm. pressure; about a 10 per cent. yield of 1-methylcoumaranone, $C_6H_4<\begin{matrix}O-\\CO\end{matrix}>CHMe$, is obtained when it is condensed with benzene in the presence of aluminium chloride. 1-*Methylcoumaranone* is a yellowish oil which boils at 163—165° under 40 mm. pressure, is volatile with steam, and reduces Fehling's and ammoniacal silver oxide solutions. R. H. P.

Syntheses by means of Organo-magnesium Compounds. Joseph Houben and Ludwig Kesselkaul (*Ber.*, 1902, **35**, 3695—3696).—Pinene hydrochloride, when dissolved in ether and treated first with magnesium and then with carbon dioxide, yields an *acid*, $C_{10}H_{17}\cdot CO_2H$, which boils at 156° under 12 mm. pressure. Carbon disulphide reacts with benzyl magnesium chloride forming *dithiophenylacetic acid*, $CH_2Ph\cdot CS_2H$, which is a reddish-yellow oil, has an unpleasant odour, is somewhat soluble in water, and distils under 5 mm. pressure, decomposing to some extent. R. H. P.

Hydroxycamphor. Otto Manasse (*Ber.*, 1902, **35**, 3811—3828. Compare Abstr., 1897, i, 290).—A modified method is given of preparing α-hydroxycamphor (*loc. cit.*) by reducing camphorquinone with zinc dust and acetic acid; the compound is soluble in water, melts at 203—205°, and, contrary to the previous statement, possesses acid properties; the *sodium* and *potassium* salts separate in glistening flakes when the substance is covered with 50 per cent. sodium or potassium hydroxide and shaken with ether; the dry substance, unlike its solution, decomposes spontaneously to a thick, honey-like mass containing camphoric acid. The *methyl* ether, $C_8H_{14}<\begin{matrix}CH\cdot OMe\\|\\CO\end{matrix}$, gradually separates in prismatic crystals from a solution of hydroxycamphor in anhydrous methyl alcoholic hydrogen chloride; the further action of the hydrogen chloride converts the ether into an oily compound (? isomeride); the ether has no taste or odour, is insoluble in water, crystallises from methyl alcohol in glistening prisms, and melts at 149—150°. The *ethyl* ether crystallises from alcohol in four-sided tablets, melts at 85—86°, and is more soluble than the methyl ether. An oily isomeride is also produced by the further action of the alcoholic hydrogen chloride on the ether; this boils at 231—232° under 714 mm. pressure, is colourless, and has an odour suggestive of camphor and peppermint; unlike the solid

isomeride, it is not readily hydrolysed by strong hydrochloric acid, is stable towards hydrobromic acid and sodium hydroxide, and is only slightly acted on by dilute sulphuric acid at 130°. When hydrolysed by hydrochloric, hydrobromic, or dilute sulphuric acid (at 130°), ethoxycamphor is converted into *β-hydroxycamphor*, isomeric with that previously described; this is more stable than the α-isomeride, melts at 212—213°, has $[\alpha]_D$ +12·3° in alcohol (α-hydroxycamphor melts less sharply at 203—205°, a mixture melts at 207—209°, and a mixture crystallised from light petroleum at 204—206°), is readily converted into the methyl ether described above, and is oxidised by chromic acid to camphorquinone; the two compounds and the mixture separate from light petroleum in feathery forms which cannot be distinguished, and the α-compound yields no trace of the β- when left for several days in contact with strong hydrochloric acid. The *oxime* of β-hydroxycamphor crystallises from light petroleum in three-sided tablets (the α-oxime is less soluble in light petroleum, separates in prisms, and melts at 86—87°). The *β phenylhydrazone* melts at 111—113° (α-phenylhydrazone at 137·5°, mixture at 91—92°), is more soluble in dilute alcohol than the α phenylhydrazone, from which it also differs in the readiness with which it separates as an oil, and crystallises in pyramidal forms. The *β semicarbazone* is more soluble in alcohol than the α-compound, and melts at 202—204° (α at 182—183°, mixture at 170—172°). The *β-benzenesulphonate* separates from alcohol in tabular crystals (α in pyramids) and melts at 111—113° (α at 95—96°, mixture at 92—93°); an *isomeric benzenesulphonate* is also produced which crystallises in hexagonal tablets and melts at 79—80°. Both α- and β-hydroxycamphor are readily reduced by sodium amalgam to a camphor which yields an oxime and semicarbazone of normal melting point, but that from α-hydroxycamphor has $[\alpha]_D$ +11·45° only, whilst β-hydroxycamphor yields an almost inactive camphor, $[\alpha]_D$ +1·3°.

Hydroxycamphor is reduced by sodium and alcohol to *camphorglycol*, $C_8H_{14}<\begin{smallmatrix}CH\cdot OH\\|\\CH\cdot OH\end{smallmatrix}$, which separates from light petroleum in glistening flakes, melts at 230—231°, has $[\alpha]_D$ +12·3° in alcohol, dissolves in 200 parts of cold water, sublimes readily, is volatile with steam, has a slightly bitter, camphor-like taste, is oxidised by chromic acid to camphorquinone and (?) hydroxycamphor, and by dilute permanganate to camphoric acid. The *phenylurethane*, $C_{24}H_{28}O_4N_2$, separates as a crystalline powder from benzene or light petroleum, melts at 161—163°, and yields an odour of *iso*nitrile when acted on by sodium hydroxide. When heated with dilute sulphuric acid, the glycol loses water, but is not altered by heating with water to 200°; the product has the composition of a camphor, and contains a little ordinary camphor, but consists chiefly of an oil, of which half distilled between 206° and 211° under 724·6 mm. pressure; it yielded a small amount of bisulphite compound, and this, when heated with soda, gave an oil of peppermint-like odour. Hydrochloric acid converts the glycol into a *chlorohydrin* melting at 110—113°.

T. M. L.

Study of Aminocamphor. ALFRED EINHORN and STEPHAN JAHN (*Ber.*, 1902, 35, 3657—3668).—*Ethyl camphorylglycinate*,

$C_6H_{14}<\begin{matrix}CH\cdot NH\cdot CH_2\cdot CO_2Et\\ | \\ CO\end{matrix}$, prepared by heating aminocamphor with ethyl chloroacetate, is a colourless, mobile oil; its *hydrochloride* crystallises in small needles, decomposes at 188°, and has a toxic effect when introduced intravenously into a rabbit. The *nitrosoamine* crystallises from petroleum in yellow leaflets melting at 105°; it gives the Liebermann reaction.

Dicamphorylamine, $NH\left(CH<\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}\right)_2$, results from the interaction of aminocamphor, chloroacetic acid, and anhydrous sodium carbonate on the water-bath; it sinters at 160°, decomposes at 181—182°, and crystallises in needles from ether or petroleum.

The compound is a weak base, the solutions of its salts having an acid reaction; it is not affected by ferric chloride or nitric acid, and has not been acetylated. The *hydrochloride* and *sulphate* crystallise from alcoholic solutions, on the addition of alcohol, in needles melting respectively at 220—222° and 212°; the picrate forms yellow leaflets melting at 185°.

The *nitrosoamine*, $NO\cdot N\left(CH<\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}\right)_2$, crystallises from alcohol in needles and melts at 190°; the product of the action of phenylhydrazine could not be crystallised.

Diborneolamine (*di*-1 : 1-*hydroxycamphanylamine*),

$$NH\left(CH<\begin{matrix}C_8H_{14}\\ | \\ CH\cdot OH\end{matrix}\right)_2,$$

produced by reducing the preceding base with alcohol and sodium, crystallises from petroleum in needles sintering at 195° and melting at 197°; it volatilises without decomposition, and yields a *sulphate* and a *nitrosoamine* which crystallise in needles.

Dicampheneisopyrazine, $C_{20}H_{28}N_2$, is a bye-product of the condensation of aminocamphor and its hydrochloride at 220—230°; the chief product of this reaction is the isomeric dicamphenepyrazine, camphor and camphorquinone being simultaneously formed. The new compound, separated from its isomeride by fractional crystallisation from acetone, forms well-defined, bitetragonal prisms with pyramidal terminations, melts at 202—203°, and volatilises at higher temperatures without decomposition; it is a very stable substance and is not affected by acid chlorides, oxidising agents, concentrated sulphuric acid, piperidine, or alcoholic potassium hydroxide. The *picrate*, $C_{20}H_{28}N_2,C_6H_3O_7N_3$ crystallises from alcohol in yellow needles melting at 203°; the *mercurichloride*, $C_{20}H_{26}N_2,HgCl_2$, is a white, curdy precipitate, crystallising from alcohol in needles melting at 236°. Duden and Pritzkow (Abstr., 1899, i, 779) found that dicamphenepyrazine forms the double salt $C_{20}H_{28}N_2,2HgCl_2$.

Dicampheneisopyrazine methiodide, $C_{20}H_{28}N_2$,MeI, dissolves in water to a colourless solution, but crystallises therefrom in yellow needles decomposing into its generators above 260°. G. T. M.

Camphonitrophenol. GIACOMO PONZIO (*Gazzetta*, 1902, 32, ii, 34—36).—A readier method for the preparation of camphonitrophenol

than that given by Cazeneuve (Abstr., 1889, 618) consists in the gradual addition of *iso*nitrosocamphor to nitric acid of sp. gr. 1·37; when the reaction is over, the liquid is diluted with water, rendered alkaline with ammonia, treated with excess of calcium chloride solution, and the well-washed calcium salt decomposed by means of dilute hydrochloric acid. The anhydrous compound melts at 225° (Cazeneuve gave 220°). T. H. P.

Reactions of Camphorquinone. Otto Manasse and Ernst Samuel (*Ber.*, 1902, 35, 3829—3843. Compare Abstr., 1898, i, 147; 1899, i, 300; Bredt, Abstr., 1902, i, 217).—The ketonic acid obtained by the action of sulphuric acid on camphorquinone is not oxidised to camphoric acid, yields no formic acid or carbon dioxide when heated with sulphuric acid or carbon dioxide, is stable towards alkalis and mineral acids, and is therefore probably a γ- or δ-ketonic acid. The acid crystallises in rhombic prisms [$a:b:c = 0·9030:1:0·4275$], melts at 97—98°, and distils at 297—302° with only slight decomposition. The *methyl* ester separates from methyl alcohol in large, brilliant, monoclinic tablets [$a:b:c = 2·225:1:4·275$; $\beta = 93°55'$], melts at 82—83°, and can be crystallised from much hot water; its *phenylhydrazone* crystallises from acetic acid and melts at 99—100°. The *ethyl* ester is a colourless oil of menthol-like odour and boils at 250°. The *hydroxy*-acid, $C_{10}H_{18}O_3$, prepared by reducing with sodium amalgam, crystallises from water in long, silky needles with $1H_2O$ and becomes anhydrous when heated at 80°; the anhydrous acid crystallises from benzene and melts at 133—134°.

The *iso*camphorquinone, which is also produced by the action of sulphuric acid on camphorquinone, was first regarded as the enolic form of the quinone, was then shown by Bredt to contain the $:CMe_2$ group, and is now formulated as $\Delta^{1,4}$ (8)-terpadienol (2) or (3),

$$CMe{<}\begin{matrix}C(OH)\cdot CO\\ CH_2—CH_2\end{matrix}{>}C:CMe_2.$$

It is stable when kept in a vacuum over sulphuric acid, but when heated to 50° softens and liberates pungent fumes of acetic acid like odour. It behaves as a stable hydroxy-ketone and has no tendency to react as a diketone. The *copper* salt, $(C_{10}H_{13}O_2)_2Cu$, is a green powder and soon decomposes in the air. The *oxime* crystallises from benzene or light petroleum and melts at 122—133°. The *phenylhydrazone* crystallises from alcohol and melts at 169—170°. The *benzoyl* derivative separates from light petroleum in large, monoclinic crystals [$a:b:c = 1·325:1:0·965$; $\beta = 146°38'$] and melts at 79°. The *phenylurethane* solidifies in needles, has no sharp melting point, and is decomposed by boiling with alcohol. With *o*-phenylenediamine, the hydroxyketone condenses with elimination of only one mol. of water; the *product*, $C_{16}H_{20}ON_2$, separates from light petroleum in colourless needles, melts at 122—123°, and gives a *nitrosoamine* melting at 114°. The *nitroso*-compound (nitrite) is a white powder and melts and decomposes at 142—143°. The *hydrobromide*, $C_{10}H_{15}O_2Br$, crystallises from acetic acid in large tablets, melts and decomposes at 163°, and is resolved into its components by cold water. The *hydrochloride*, prepared by covering the hydroxyketone with concen-

trated hydrochloric acid, melts and decomposes at 130—133° and is as unstable as the hydrobromide.

The acid, $C_7H_{12}O_3$, prepared by boiling the acid with dilute sulphuric acid, is not identical with Dieckmann's β-hydroxy-α-methyl*cyclo*pentanecarboxylic acid (Abstr., 1901, i, 539) or with his β-hydroxy-γ-methyl*cyclo*pentanecarboxylic acid; it is oxidised to succinic acid, and a ketonic acid could not be obtained by oxidising the methyl ester; it distils with formation of a small amount of unsaturated acid at 255—260°. The *silver* salt, $C_7H_{11}O_3Ag$, crystallises in small needles. T. M. L.

The Essence of the Wood of Atlas Cedar. ÉMILIEN GRIMAL (*Compt. rend.*, 1902, **135**, 582—583).—The oil obtained from *Cedrus Atlantica* and *Cedrus Libani* with steam was distilled under 16 mm. pressure, and six fractions were collected between 50° and 175°. The first fraction was redistilled under the ordinary pressure; the most volatile part of it contained ordinary acetone, but between 180° and 215° an oil was obtained which possessed exactly the odour of the original essence, and contained a ketone of the formula $C_9H_{14}O$. This ketone gave a semicarbazone, $C_{10}H_{17}ON_3$, which melted at 159—160°; its oxime was not obtained in the solid form, but when treated with hydroxylamine hydrochloride, and then with bromine, it gave crystals of a brominated oxime, $C_9H_{15}ONBr_2$, which melted at 132—133°.

The second fraction of the original distillation gave an oil which boiled between 271° and 276° under the ordinary pressure, and has been identified as the sesquiterpene cadinene, $C_{15}H_{24}$ (Wallach, Abstr., 1887, 595).

The fifth fraction, when distilled under the ordinary pressure, gave a thick oil between 291° and 295°, which appears to contain several sesquiterpenic alcohols. J. McC.

Chinese Anise Oil. E. TARDY (*Bull. Soc. chim.*, 1902, **27**, [iii], 990—994).—This oil, when freed from most of its anethole by exposure to a low temperature, has $[\alpha]$ $-3°15'$ and was found to contain anisaldehyde and anisic acid, quinol ethyl ether, *p*-methoxyphenylacetone, *d*-pinene, *l*-phellandrene, anethole, estragol, terpilenol, a lævorotatory sesquiterpene which boils between 270° and 275° and has $[\alpha]_D$ $-5°$, and a small amount of a colourless, crystalline substance having the composition $C_{20}H_{22}O_3$, but no safrole (compare Oswald, Abstr., 1891, i, 957). The largest fractions of the oil were obtained between 174° and 180° (*l*-phellandrene) and 220° and 230° (anethole, estragol, and terpilenol). T. A. H.

Japanese Anise Oil. E. TARDY (*Bull. Soc. chim.*, 1902, **27**, [iii], 987—990. Compare Eykmann, Abstr., 1885, 95).—This oil, prepared by extraction of the seeds of *Illicium religiosum* with light petroleum has $[\alpha]_D$ $-150°$. It contains eugenol, cineol, safrole, borneol (?), and a small quantity of a substance giving anisic acid when oxidised with potassium permanganate, possibly anethole or estragol. There are also present small quantities of palmitic and other

fatty acids, but no aldehydes or esters. Eykmann's shikimene is shown to be a slightly optically active mixture of at least two terpenes, one of which furnishes terpilene hydrobromide with bromine and is probably a terpane. T. A. H.

Methyl Methylanthranilate in the Vegetable Organism. Eugène Charabot (*Compt. rend.*, 1902, 135, 580—582).—The oil obtained from the leaves of *Citrus madurensis* by distillation with steam possesses a sweet odour and has a_D $+6°40'$ in a 100 mm. tube. Its saponification coefficient is 160, but after treatment with acetic anhydride this coefficient becomes much smaller. When treated with sulphuric acid, it gives about 50 per cent. of methyl methylanthranilate, $C_9H_{11}O_2N$, in the form of crystals which melt at 19°. The compound was identified by converting it into methylanthranilic acid and its acetyl derivative. J. McC.

Oil of Bitter Fennel. E. Tardy (*Bull. Soc. chim.*, 1902, 27, [iii], 994—997. Compare Abstr., 1897, i, 578).—A specimen of this oil from Algeria had an amber-like colour, an odour recalling those of camphor and of turpentine, sp. gr. 0·991, and $[a]_D$ $+62°16'$. It contained *d*-pinene, phellandrene, fenchone, estragol (about 10 per cent.), anethole in small quantity, a sesquiterpene which boiled between 175° and 180° under 30 mm. pressure and had $[a]_D$ $-2°40'$, and a diterpene which boiled at 215° under the same pressure and had $[a]_D$ $+10°20'$.

A specimen of Galician oil was colourless, had a camphor-like odour, $[a]_D$ $+39°52'$, and when cooled to $-18°$ deposited colourless crystals. It contained a *d*-camphane, *d*-phellandrene, fenchone (in large quantity), a minute proportion of estragol, and only traces of anethole. It is supposed that the anethole had been fraudulently removed. The lower proportion of estragol in the Galician oil is regarded as due to climatic influences. T. A. H.

Ethereal Oil of Gardenia. E. Parone (*Chem. Centr.*, 1902, ii, 703—704; from *Boll. Chim. Farm.*, 41, 489—498).—Oil of gardenia is a clear, yellowish liquid which gradually decomposes when heated for a long time at 200° and boils with partial decomposition at 204°; it is readily soluble in alcohol or ether and has $[a]_D$ $+1·47°$ at 20° (50 mm. tube). In the various fractions obtained by distilling the oil under 12—15 mm. pressure, benzyl acetate, styrene acetate, linalool, linalyl acetate, terpineol, and methyl anthranilate were detected. Benzoic acid is probably also present as an ester together with other compounds which were not determined. Benzyl acetate is the main component of the oil, which owes its odour, however, to the presence of styrene acetate, $C_6H_5·CHMe·OAc$. The latter was prepared by synthetical methods; it boils and decomposes at about 215° and has a sp. gr. 1·058 at 16°. E. W. W.

German Oil of Rue and the Transformation of Methylnonylketoxime. J. Houben (*Ber.*, 1902, 35, 3587—3592).—The oil

had a slight fluorescence, which was probably caused by traces of a basic nitrogenous substance which could be extracted with acids; soda removed a small amount of free fatty acid, probably consisting of octoic acid (b. p. 236—238°). One per cent. of a phenolic substance melting at 155—156° (compare Thoms, *Ber. deut. pharm. Ges.*, 1901, 11, 3) was isolated, as well as 71 per cent. of methyl nonyl ketone and 2·4 per cent. of methyl heptyl ketone.

Methyl heptyl ketone boils at 194—196° under atmospheric and at 80—82° under 15 mm. pressure (compare Soden and Henle, Abstr., 1901, i, 396); on reduction with sodium in aqueous ether, it yields *methylheptylcarbinol*, which boils at 193—194° under atmospheric and at 90—91° under 12 mm. pressure. *Dimethylheptylcarbinol*, $C_7H_{15}\cdot CMe_2\cdot OH$, synthesised from methyl heptyl ketone and magnesium methiodide, boils at 96—98° under 13·5 mm. pressure and does not solidify at −15°.

Methyl nonyl ketone melts at 13°, boils at 228—230° under atmospheric, at 118° under 18 mm., and at 120° under 20 mm. pressure; it has a sp. gr. 0·8295 at 15°, 0·8263 at 20° (compare Thoms and Soden and Henle, *loc. cit.*).

On reduction with sodium, *methylnonylcarbinol* and *methylnonylcarbinolpinacone* are obtained; the carbinol boils at 115° under 10 mm. and at 120° under 14 mm. pressure, and its *acetate* at 122° under 11 mm. pressure; the *pinacone*, $C_{22}H_{46}O_2$, is solid at the ordinary temperature and boils at 215° under 10 mm. pressure. *Dimethylnonylcarbinol*, obtained by the Grignard reaction, boils at 117—118° under 12·5 mm. pressure.

Thoms, working with methylnonylketoxime, has confirmed Hantzsch's law for the transformation of ketoximes, by which the alkyl radicle of greater molecular weight changes place with the hydroxyl group of the *iso*nitroso-group; the author, however, finds that with concentrated sulphuric acid methylnonylketoxime yields at least 30 per cent. of decomethylamide, a fact quite out of accord with Hantzsch's view. W. A. D.

Colouring Matter of the Red Grape. II. Livio Sostegni (*Gazzetta*, 1902, 32, ii, 17—19. Compare Abstr., 1898, i, 331).—On treating the red colouring matter previously described (*loc. cit.*) with potassium hydroxide, either in the fused state or in 30 per cent. solution, the principal product obtained is protocatechuic acid, small quantities of catechol and another phenol, probably hydroxyquinol, also being formed.

The *acetyl* derivative of the colouring matter, $C_{19}H_9O_9Ac_5$, deposited after a year from a concentrated acetic acid solution of the substance, is a bright red, crystalline powder, slightly soluble in alcohol and more so in solutions of the alkalis, to which it imparts a dark red coloration. The *benzoyl* compound, $C_{19}H_9O_8Bz_5$, prepared by the action of sodium hydroxide and benzoyl chloride on the potassium compound (*loc. cit.*), is an amorphous substance soluble in alcohol.

The author regards the colouring matter as a kind of tannin derived

from protocatechuic acid and ascribes it to the following formula: $C_6H_3(OH)_2 \cdot CO \cdot O \cdot C_6H_3(OH) \cdot O \cdot C_6H_3(OH)_2$. T. H. P.

Benzidine-blue and some Reactions of Benzidine. G. Saget (*Chem. Centr.*, 1902, ii, 897—898; from *Mon. Scient.*, [iv], 16, ii, 655—656).—When a cold aqueous solution of potassium permanganate is added to a cold aqueous solution of benzidine hydrochloride, a blue precipitate is formed which becomes darker as the addition of the permanganate proceeds, until it finally attains a deep indigo-blue colour The precipitate is not quite insoluble in water, and is decomposed by the addition of more permanganate. The reaction does not take place in presence of hydrochloric acid. Sulphuric acid throws down a white precipitate of benzidine sulphate from a solution of the hydrochloride, and this, when treated with potassium permanganate, becomes yellow. By the action of finely divided manganese dioxide on an excess of benzidine hydrochloride and a small quantity of water, a dark blue precipitate is formed which is very sparingly soluble in cold water and is decomposed by hydrochloric acid, ammonia, or sodium carbonate, or by heating with water at 65°.
E. W. W.

A Derivative of Hydrogen Peroxide [Dinaphthapyranol]. Robert Fosse (*Compt. rend.*, 1902, 135, 530—533).—Dinaphthapyranol (Abstr., 1902, i, 689) is reduced by zinc powder to colourless bis-dinaphthapyryl (bis-dinaphthaxanthene), identical with that obtained in the same way from dinaphthapyryloxonium. The dinaphthapyranol, dissolved in acetic acid, oxidises alcohol with formation of aldehyde and dinaphthapyran, oxidises pyrogallol, and liberates the whole of the iodine from potassium iodide. These facts show that the dinaphthapyranol is not an alcohol but a derivative of hydrogen peroxide of the constitution $CH{<}^{C_{10}H_6}_{C_{10}H_6}{>}O \cdot OH$, one of the oxygen atoms being quadrivalent. C. H. B.

Synthesis of Benzopyrone. E. Rap (*Gazzetta*, 1902, 32, ii, 53—57).—Owing to the appearance of papers on this subject by Ruhemann with various other authors, the author gives the incomplete results of a continuation of his previous work (see Abstr., 1896, i, 303).

The condensation of sodium phenoxide with ethyl chlorofumarate yields a *substance* boiling at 142—143·5° under 5 mm. pressure, and on hydrolysis with barium hydroxide giving rise to an *acid* separating from water in small crystals melting at 211°. These compounds are considered by the author to be identical with Ruhemann's ethyl phenoxyfumarate, boiling at 183—184° under 14 mm. pressure, and the corresponding acid melting at 215° (see Trans., 1900, 77, 1121).
T. H. P.

Nitropyromucic Acid and its Ethyl Ester. Dinitrofurfuran. R. Marquis (*Compt. rend.*, 1902, 135, 505—507).—By the nitration of ethyl pyromucate by the method previously described for fur-

furan (Abstr., 1901, i, 222), a yellow liquid is formed, which, on treatment with pyridine, gives yellow crystals of ethyl nitropyromucate which melt at 101°. When saponified, by heating with water at 180°, nitropyromucic acid is formed. This contains the nitro-group either in the 3- or 4-position, and, since it is identical with the nitropyromucic acid described by Hill and White (Abstr., 1902, i, 388), they are incorrect in stating that their compound contains the nitro-group in the 5-position.

3-Nitrofurfuran, on nitration, gives a dinitrofurfuran identical with the compound obtained by Hill and White (*loc. cit.*), and the constitution given by them must be modified so as to account for the presence of one nitro-group in the 3-position. J. McC.

Thionaphthen contained in Brown-Coal Tar. JOHANNES BOES (*Chem. Centr.*, 1902, ii, 804; from *Apoth.-Zeit.*, **17**, 565).—Thionaphthen has been isolated from the fraction of brown-coal tar boiling at 215—225° by precipitation as the picric acid compound. The purified thionaphthen melts at 30—31°, combines with bromine in the cold, and readily forms bromo-derivatives.

Peat tar and American crude petroleum do not contain thionaphthen. E. W. W.

Acyl Derivatives of Cinchona Alkaloids. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 131723).—The acyl derivatives of the cinchona alkaloids are prepared by the action of the phenyl esters of the organic acids on these bases. The reaction is conveniently effected in benzene solution, and the phenol set free is separated from the acyl compound by shaking the product with dilute sodium hydroxide solution.

Anisylquinine, $C_{20}H_{23}ON_2 \cdot O \cdot CO \cdot C_6H_4 \cdot OMe$, forms white needles melting at 87—88°.

Salicylquinidine and salicylquinine may also be isolated by this process providing that very dilute sodium hydroxide solution is employed in extracting the phenol. G. T. M.

Rotatory Power of Cocaine Hydrochloride. HENRI IMBERT (*Bull. Soc. chim.*, 1902, **27**, [iii], 985—987. Compare Antrick, Abstr., 1887, 506, and Hérissey, Abstr., 1898, i, 498).—Determinations of the specific rotatory power of cocaine hydrochloride in aqueous solution at 17° show that for concentrations (c) between 2 and 20 per cent. this constant can be calculated from the formula $[\alpha]_D - (71 \cdot 5776 - 0 \cdot 3788c)$. In water-alcohol solution, the specific rotatory power for concentrations (c) between 2 and 8 per cent. is given by the expression $[\alpha]_D - (68 \cdot 77 - 0 \cdot 225c)$. When the alcohol employed contains less than 35 per cent. of water, the specific rotatory power of the salt becomes constant and equal to $-67 \cdot 5°$. T. A. H.

Alkaloids of Calumba Root (Jateorrhiza Columba *syn.* Cocculus Palmatus. JOHANNES GADAMER (*Arch. Pharm.*, 1902, **240**, 450—453).—In view of Gordin's statement (Abstr., 1902, ii,

368) that *Cocculus palmatus* contains no berberine, a preliminary examination of *Radix Calumba* has been made. It is found that: (1) Calumba root contains at least two alkaloids which resemble berberine, but are not identical with it. (2) These alkaloids are yellow; when reduced, they yield colourless hydro-compounds, which can be extracted with ether, unlike the parent substances. (3) Berberine itself is probably not contained in the root. (4) The alkaloids, like berberine, are probably quaternary bases, and the hydro-compounds which they yield when reduced are probably tertiary bases.
C. F. B.

Scopolamine and Scopoline. Ernst Schmidt (*Chem. Centr.*, 1902, ii, 844—845; from *Apoth.-Zeit.*, **17**, 592—593. Compare Abstr., 1898, i, 499).—When scopoline, $C_8H_{13}O_2N$, is heated with four times its weight of hydriodic acid of sp. gr. 1·9 and a small quantity of red phosphorus at 150°, *hydriodoscopoline hydriodide*, $C_8H_{14}O_2NI,HI$, is formed; by the action of the same reagents at 190°, however, the base *hydroscopoludine*, $C_8H_{15}N$, is obtained together with methylamine and a liquid hydrocarbon which has the odour of petroleum. The hydriodide separates from water in colourless crystals, and is only sparingly soluble in cold water. *Hydrobromoscopoline hydrobromide*, $C_8H_{14}O_2NBr,HBr$, prepared by heating scopoline for six hours at 130° with four times its weight of a solution of hydrobromic acid saturated at 0°, crystallises from water or dilute alcohol in colourless, columnar crystals or plates, melts at 202°, and is rather sparingly soluble in water or alcohol. The *aurichloride* of the *diacetyl* derivative, $C_8H_{12}NBr(OAc)_2,HAuCl_4$, crystallises from alcohol in golden-yellow plates, and melts at 187°. When hydrobromoscopoline is reduced with zinc and sulphuric acid, a compound is formed which also yields a diacetyl derivative. The *aurichloride* of the latter, $C_8H_{13}N(OAc)_2,HAuCl_4$, crystallises from alcohol in leaflets and melts at 185°.

The benzoyl derivative of the reduction product of hydrobromoscopoline forms an *aurichloride*, $C_8H_{13}N(OBz)_2,HAuCl_4$, which crystallises from alcohol in transparent, nodular masses and melts at 200—201°.

Hydroxylamine, phenylhydrazine, semicarbazide, &c., do not react with scopoline.

From the foregoing reactions, it is evident that scopoline must contain a group $O<\begin{matrix}C=\\|\\C=\end{matrix}$, which, by the action of hydrobromic or hydriodic acid, is converted into the group $\begin{matrix}HO\cdot C=\\|\\BrC=\end{matrix}$.
E. W. W.

Action of Sulphuryl Chloride on Pyrrole. II. Girolamo Mazzara (*Gazzetta*, 1902, **32**, ii, 28—33. Compare Abstr., 1902, i, 820).—The action of excess of sulphuryl chloride on an ethereal solution of pyrrole at 0° gives an almost theoretical yield of the pentachloropyrrole obtained by Anschütz and Schroeter (Abstr., 1897, i, 367). As obtained by the author, this compound boils at 209° under

the ordinary pressure and at 142° under 15 mm. pressure; it gives the normal molecular weight in freezing benzene. The action of water, especially when hot, yields dichloromaleimide. The same pentachloropyrrole is obtained by the action of sulphuryl chloride on an ethereal solution of tetrachloropyrrole.

The author regards the formation of dichloro- or dibromo-maleimide by the action of hypochlorites or hypobromites on pyrrole, tetrachloro-, or tetrabromo-pyrrole not as direct oxidation processes, but as due to the intermediate formation of a pentahalogenated pyrrole, which is then decomposed by water, yielding the di-substituted maleimide.

T. H. P.

Action of Phosphorus Pentachloride on 1-Alkylpyridones and 1-Alkylquinolones. IV. OTTO FISCHER (*Ber.*, 1902, **35**, 3674—3683. See Abstr., 1899, i, 635).—[With THEODOR MERL.]—2-p-*Methoxyanilinopyridine*, obtained when 2-chloropyridine, *p*-anisidine, and zinc chloride are heated in a sealed tube for five hours at 220—230°, crystallises from light petroleum in small leaflets, melts at 85°, and gives a violet coloration with sulphuric acid. The *aurichloride* crystallises in red prisms melting at 150°, the *platinichloride* is a canary-yellow, microcrystalline powder which melts at 188°, and the *mercurichloride* crystallises in needles and is soluble in hydrochloric acid. 2-o-*Methoxyanilinopyridine* crystallises from light petroleum in flat plates melting at 63—64°, 2-p-*ethoxyanilinopyridine* from alcohol in colourless needles melting at 94°, 2-α-*naphthylaminopyridine* crystallises from alcohol in colourless needles melting at 115°, and the corresponding *β-compound* in white leaflets melting at 133°. *o*- and *p*-Aminobenzoic acids, when condensed under similar conditions, evolve carbon dioxide and yield 2-anilinopyridine. *Di-2-pyridyl-*o-*phenylenediamine* crystallises from alcohol in small, white leaflets, melts at 166—167°, and forms a crystalline *platinichloride* and a *dinitrosoamine*, which crystallises in bright yellow prisms and melts at 136°. *Di-2-pyridyl-*p-*phenylenediamine* crystallises in white needles, melts at 200—201°, and forms a yellow, crystalline *platinichloride* and *aurichloride*. The corresponding *meta*-derivative was obtained in slender white needles melting at 160°.

1-*Methylthiopyridone methiodide*, $C_5NH_4Me\colon SMeI$, obtained as a mass of yellow needles when methyl iodide is added to 1-methylthiopyridone, melts at 156°, and, when treated with sodium hydroxide, yields methyl mercaptan. The corresponding *ethiodide* was obtained as a yellow oil, which solidified when rubbed. 1-*Methylthioquinolone methiodide* separates from alcohol in compact, yellow crystals and melts at 189°; the *allyl iodide* crystallises in orange-yellow prisms and melts and decomposes at about 180°.

[With P. DREVERHOFF.]—1 : 8-Dimethylquinolone, when heated with phosphorus pentachloride, yields 2-*chloro*-8-*methylquinoline*, which crystallises in colourless needles, melts at 61°, and boils at 286° under 734 mm. pressure. The *hydrochloride* crystallises in long needles, the *sulphate* is only slightly soluble in water, the *platinichloride* crystallises in long, yellow needles, the *aurichloride* in orange-yellow needles, the *mercurichloride* was obtained as a flocculent precipitate, and the *picrate* crystallises in

long, yellow needles. 2-*Amino-8-methylquinoline*, obtained by heating the chloro-compound with ammonio-zinc chloride, crystallises from water in bright yellow, felted needles. When the chloro-compound is nitrated, a 2-*chloronitro-8-methylquinoline* is obtained; this crystallises in yellow, laminated prisms melting at 232°, and, when reduced, yields the corresponding *amino*-compound which crystallises from light petroleum in light yellow prisms and melts at 148°.

[With R. BERCKHEMER and J. ULBRICHT.]—8-*Methoxy*-1 *methylquinoline* crystallises from alcohol in colourless, iridescent plates, melts at 70°, and, when treated with phosphorus pentachloride, yields 2-*chloro-8 methoxyquinoline*, which crystallises in colourless plates and melts at 82°. The *hydrochloride* crystallises in colourless needles, the *mercurichloride* in voluminous, felted needles, and the *platinichloride* forms compact, golden-yellow crystals.

2-*Amino-8-methoxyquinoline* crystallises in silvery, colourless, small needles, melts at 156°, and forms an *aurichloride* which crystallises in red-brown needles. 2 *Methylamino-8-methoxyquinoline* crystallises from light petroleum in colourless, silvery prisms melting at 151° and forms a crystalline *nitrosoamine* which melts at 180°. 2-*Thiol-8 methoxyquinoline* crystallises from alcohol in beautiful, yellow prisms, melts at 211°, and forms a crystalline *mercurichloride*.

2-*Chloro-6-bromoquinoline* crystallises in small, white needles, and melts at 159—160°. 6-*Bromo-2-thiolquinoline* melts at 252°. 6-Chloro-1-methyl-2-quinolone crystallises in clusters of needles, melts at 150°, and reacts with phosphorus pentasulphide, forming 8-*chloro-2-thiolmethylquinolone*, which crystallises in greenish needles melting at 184°, and yields additive compounds with alkyl iodides. 2 : 6-*Dichloroquinoline*, crystallises in slender, white needles, melts at 156°, and is feebly basic; the corresponding 6-*chloro-2-aminoquinoline* crystallises in white needles, melts at 152°, and forms an *aurichloride* which crystallises in golden-yellow needles. 7-*Chloro*-1-*methyl-2-quinolone* crystallises in short, white needles melting at 139—140°, and 2 : 7-*dichloroquinoline* in colourless, felted needles melting at 98—99°. R. H. P.

Condensation of Isatic Acid to Cinchonic Acid and its Derivatives. WILHELM PFITZINGER (*J. pr. Chem.*, 1902, [ii], **66**, 263—264. Compare Abstr., 1898, i, 207).—Isatic acid condenses with acetaldoxime in presence of potassium to form cinchonic acid and the oxime of isatic acid. With *iso*nitrosoacetone, isatic acid forms the *oxime* of α-aldehydocinchonic acid, which crystallises in greyish-yellow leaflets and melts at 251°. With acetyl chloride, the oxime forms an *acetate* which melts at 195° and decomposes into acetic acid and 2-*cyanocinchonic acid*. 2-Cyanocinchonic acid crystallises in long needles, melts at 226°, and is easily hydrolysed to quinoline-2 : 4-dicarboxylic acid.

o-Aminobenzaldehyde condenses with *iso*nitrosoacetone to form the oxime of 2-aldehydoquinoline, which crystallises in delicate, white needles, melts at 189°, is acetylated by acetic anhydride, and yields 2-cyanoquinoline melting at 93°. G. Y.

Interaction of Kairoline with Esters of Iodoacetic Acid. EDGAR WEDEKIND and ROBERT OECHSLEN (*Ber.*, 1902, **35**, 3580—3586. Compare Abstr., 1902, i, 277).—Kairoline interacts at the ordinary temperature with ethyl iodoacetate, giving ethyl kairoliniumiodoacetate, $C_9H_{10}NMeI\cdot CH_2\cdot CO_2Et$, along with kairoline hydriodide and methiodide; with methyl iodoacetate, methyl kairoliniumiodoacetate is obtained with the same bye-products. The kairoline hydriodide is probably formed by the elimination of hydrogen iodide from two mols. of the iodoacetic ester, a maleic or fumaric ester being produced; the methiodide may be produced by double dissociation (compare Abstr., 1902, i, 392), or more probably by a stereochemical change.

Kairoline hydriodide forms monoclinic crystals [$a:b:c = 1\cdot1023:1:1\cdot3274$; $\beta = 71°53'$] and kairoline methiodide orthorhombic prisms [$a:b:c = 0\cdot8386:1:0\cdot5319$]. W. A. D.

Dinitrocarbazolesulphonic Acid. ERNST WIRTH & HEINRICH SCHOTT (D.R.-P. 128854).—*Dinitrocarbazolesulphonic acid*, prepared by the prolonged action of excess of concentrated sulphuric acid on dinitrocarbazole (Abstr., 1902, i, 495) at 95—100°, is separated from the disulphonic acid by diluting the product until it has a sp. gr. of 1·3—1·4. Under these conditions, the monosulphonic acid is completely precipitated, whilst the disulphonic acid remains in solution. The former is dissolved in hot water and precipitated from the solution in the form of its sodium salt by the addition of excess of sodium chloride. This sulphonation apparently leads to the formation of two monosulphonic acids, one of which, the α-acid, has been purified by taking advantage of the sparing solubility of its alkali, calcium, and ammonium salts. G. T. M.

4-Nitro-*m*-phenylenediamine. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 130438).—*p*-Nitroaniline-3-sulphonic acid, when heated with 25 per cent. ammonia solution at 170—180°, yields 4-nitro-*m*-phenylenediamine (m. p. 161°). G. T. M.

Phenylhydrazides of Organic Acids. CARL BÜLOW (*Ber.*, 1902, **35**, 3684—3691).—Ethyl phenylhydrazino-oxalate can be separated from oxalyldiphenylhydrazide by extraction by hot water; it dissolves in dilute sodium hydroxide solution, being reprecipitated by acetic acid or carbon dioxide, and is decomposed by long continued boiling with water. The *nitroso*-derivative crystallises from a mixture of chloroform and light petroleum and melts and decomposes at 80—81°. Oxamic phenylhydrazide also dissolves in dilute sodium hydroxide solution and is reprecipitated by carbon dioxide; the *acetyl* derivative crystallises from water in small, slender needles, melts at 221—222°, and only gives Bülow's reaction when warmed. *Methyl nitrosophenylhydrazino-oxamate* crystallises from water in clusters of long, white, slender needles and melts at 115—116°. *Ethyl phenylhydrazino-oxamate* crystallises in lustrous, rhombic laminæ melting at 181—182° and forms a yellow *nitrosoamine*, which melts at 107—108°. Oxalyldiphenyl-

hydrazide can easily be crystallised from a dilute solution of sodium hydroxide; the *diacetyl* derivative separates from water in heavy, granular, white crystals. The *diacetyl* derivative of succinyldiphenylhydrazide crystallises from dilute acetic acid, melts at 197°, and is more soluble in dilute sodium hydroxide solution than the hydrazide itself. R. H. P.

Pyruvylpyruvic Ester Derivatives. II. Stereoisomeric Hydrazones. LOUIS J. SIMON (*Compt. rend.*, 1902, 135, 630—631. Compare Abstr., 1902, i, 422).—By the action of concentrated sulphuric acid and aniline on ethyl pyruvate, a phenylimino-derivative of the formula $NPh{:}CMe{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$ is obtained (*loc. cit.*). In order to establish the ketonic nature of this, the action of phenylhydrazine on it has been studied. Two phenylhydrazones are formed, the *a-phenylhydrazone* being produced in the larger quantity. It melts at 195—196° and crystallises in yellow, hexagonal plates with $1H_2O$ which it loses at 110°. The β-phenylhydrazone crystallises without water in golden needles which melt at 133°. Both hydrazones are insoluble in water, potassium hydroxide solution, and concentrated hydrochloric acid, but are soluble in the common organic solvents. When the a-phenylhydrazone is heated for some time near its melting point, it is transformed into a mixture of the two hydrazones; the extent of the conversion into the β-phenylhydrazone depends on the temperature. The β-phenylhydrazone may be transformed into the a-isomeride by dissolving in alcohol and passing a current of hydrogen chloride through the solution. When the β-derivative is saponified, it gives the same acid as that obtained from the a-phenylhydrazone; this acid crystallises in slender needles which decompose at 151—152° and give the a-phenylhydrazone on esterification. The simultaneous production of the two phenylhydrazones and their mutual transformations are characteristic of stereoisomerides.

By the action of concentrated sulphuric acid on the two phenylhydrazones a brownish coloration is first developed which becomes blue. This is due to the formation of a substance which can be precipitated by pouring on to ice, but its nature has not been established.

Precisely the same results are obtained with corresponding substituted pyruvylpyruvic esters. Thus from the tolylimino-compound, $C_6H_4Me{\cdot}N{:}CMe{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$, by the action of phenylhydrazine, an *a-phenylhydrazone* melting at 175—176° is obtained which crystallises with $1H_2O$, and a β-phenylhydrazone which melts at 117—118°. J. McC.

Action of Tetrazoic Chlorides on Ethyl Oxalacetate. J. RABISCHONG (*Bull. Soc. chim.*, 1902, 27, [iii], 982—985).—*Ethyl diphenyldihydrazone-oxalacetate*, $C_{12}H_8[N_2H{:}C(CO_2Et){\cdot}CO{\cdot}CO_2Et]_2$, prepared by the addition of an aqueous solution of diphenyltetrazochloride to an alcoholic solution of ethyl oxalacetate, forms carmine-red crystals which melt at 130—131°.

Ethyl ditolyldihydrazone-oxalacetate, similarly prepared, separates from xylene in red crystals melting at 194—195°.

Ethyl dianisyldihydrazone-oxalacetate, similarly prepared from diazotised anisidine, forms yellow crystals which melt at 224—225°.

T. A. H.

Action of Phosphorus Oxychloride on Acetylanthranilic Acid. RICHARD ANSCHÜTZ and O. SCHMIDT (*Ber.*, 1902, **35**, 3463—3470. Compare Abstr., 1893, i, 166).—An acidic substance, $C_{18}H_{14}O_4N_2$, provisionally termed *bis-anhydroacetylanthranilic acid,* is produced by the action of phosphorus oxychloride on ethyl acetylanthranilate or acetylanthranil. When crystallised from glacial acetic acid, the acid separates as a pale yellow powder melting at 249—250°; it is very sparingly soluble in the other ordinary organic solvents, and dissolves in solution of sodium carbonate, sodium acetate or ammonia, or in pyridine. When heated with zinc dust, it yields aniline and benzonitrile; by the action of heat alone, acetic and benzoic acids are produced. Titrations of the substance with standard sodium hydroxide in dilute alcoholic solutions indicate that it is a dibasic acid; its alkali salts undergo hydrolysis in aqueous solutions. The *basic copper* salt, $C_{18}H_{13}O_4N_2\cdot Cu\cdot OH$, is a dark green powder, the *ammonium* salt crystallises in white needles decomposing at 239°.

The alkyl esters have the general formula $C_{18}H_{13}O_4N_2R$, and are obtained by treating with an alcohol the crude product of the action of phosphorus oxychloride on acetylanthranilic acid in toluene solution. The *methyl, ethyl,* and n-*propyl* esters crystallise in white needles melting respectively at 250—251°, 227—228°, and 251°; they dissolve in pyridine or glacial acetic acid, but are almost insoluble in the other organic solvents.

When phosphorus oxychloride acts on acetylanthranilic acid dissolved in hot toluene, three substances are formed, namely, bis-anhydroacetylanthranilic acid, methylketoquinazoline, and its *carboxylic acid* (compare succeeding abstracts); the last of these compounds was formerly described by Kowalski and Niementowski as anhydroethenyldianthranilic acid (compare Abstr., 1897, i, 416).

2-*Hydroxynaphthaleneazobenzene*-o-*carboxylic acid,*

$$OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot CO_2H,$$

the azo-compound produced by coupling diazotised anthranilic acid with β-naphthol, crystallises from glacial acetic acid in red, felted needles and decomposes at 272°; its production affords a ready means of detecting small quantities of the amino-acid.

Propyl bis-anhydroacetylanthranilate, when heated with a mixture of concentrated acetic and hydrochloric acids, yields anthranilic acid and propyl acetylanthranilate. The reactions tend to show that bis-anhydroacetylanthranilic acid may be represented either as

$$C_6H_4{<}\begin{matrix}C(OH)\colon CH\cdot CO\cdot NH\\ NH\cdot CO\cdot CH\colon C(OH)\end{matrix}{>}C_6H_4, \text{ or}$$

$$C_6H_4{<}\begin{matrix}C(OH)\cdot CH_2\cdot CO\cdot N \text{———} \\ N\text{—}CO\text{—}CH_2\text{—}C(OH)\end{matrix}{>}C_6H_4.$$

G. T. M.

Anthranil and Anthranilic Acid. RICHARD ANSCHÜTZ and O. SCHMIDT (*Ber.*, 1902, **35**, 3470—3476. Compare preceding abstract).—The physical properties of anthranil furnish evidence in support of

its lactam formula, $C_6H_4<\overset{CO}{\underset{NH}{|}}$, the molecular refractions of two specimens of the compound prepared by different methods were 33·691 and 33·672, whilst the value of M_D calculated for the lactam formula is 33·769. When pure, anthranil boils at 99—101° under 14—15 mm. pressure, and has a sp. gr. 1·1889 and n_D 1·58791 at 13·8°. The boiling points of anthranil and acetylanthranil differ by 48°, this increment being practically the same as the difference between the boiling points of methylaniline and methylacetanilide.

Acetylanthranil may be obtained by the action of boiling acetic anhydride on anthranil or acetylanthranilic acid; in the latter case, anhydroethenyldianthranilic acid (m. p. 246°) is also produced. The bye-product is also formed by heating acetylanthranilic acid alone. Anthranilic acid, when heated, partly sublimes and partly decomposes into aniline and carbon dioxide; its formyl derivative at 190—200° yields *o*-carboxyphenylketoquinazoline, $C_6H_4<\overset{CO}{\underset{N:CH}{}}>N\cdot C_6H_4\cdot CO_2H$.

G. T. M.

Action of Anthranilic Acid on Acetylanthranil. RICHARD ANSCHÜTZ, O. SCHMIDT, and A. GREIFFENBERG (*Ber.*, 1902, 35, 3477—3480. Compare preceding abstracts).—*o*-Carboxyphenyl methylketoquinazoline (m. p. 246°) is also produced by heating together acetylanthranil and anthranilic acid at 125°, N-*o*-acetylaminobenzoylanthranilic acid, $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$ (m. p. 224—225°), being formed simultaneously. These substances were respectively designated as anhydroethenyldianthranilic acid and ethenyldianthranilic acid by Kowalski and Niementowski (Abstr., 1897, i, 416). N-*o*-Acetylaminobenzoylanthranilic acid is a monobasic acid. *o*-Aminobenzoylanthranilic acid (m. p. 203°) is produced from the quinazoline by heating the latter with alcoholic potassium hydroxide solution; prolonged hydrolysis, however, leads to the formation of anthranilic acid. The quinazoline is, on the other hand, unaffected by hot hydrochloric acid. G. T. M.

Acylanthranils. RICHARD ANSCHÜTZ, O. SCHMIDT, and A. GREIFFENBERG (*Ber.*, 1902, 35, 3480—3485. Compare preceding abstracts).—The acylanthranils, $C_6H_4<\overset{CO}{\underset{N\cdot COR'}{|}}$, when treated with primary amines, NH_2R', first yield amides, $COR\cdot NH\cdot C_6H_4\cdot CO\cdot NHR^1$, which, by loss of water pass into quinazolines, $C_6H_4<\overset{CO}{\underset{N:CR}{}}>NR^1$.

Acetylanthranil and ammonia form successively acetyl-*o*-aminobenzamide (m. p. 177°) and methylketoquinazoline, $C_6H_4<\overset{CO}{\underset{N:CMe}{}}>NPh$.

2-*Methyl*-3-*phenylketoquinazoline*, $C_6H_4<\overset{CO}{\underset{N:CMe}{}}>NPh$, produced from acetylanthranil and aniline, melts at 143° and forms a *hydrochloride* crystallising from dilute hydrochloric acid in silvery-white leaflets decomposing at 276°.

3-*Hydroxy-2-methyl-4-ketoquinazoline*, $C_6H_4<\begin{matrix}CO\text{———}\\N:CMe\end{matrix}>N\cdot OH$, formed by mixing together acetylanthranil, hydroxylamine hydrochloride, and sodium carbonate in aqueous solution, crystallises from glacial acetic acid in white needles melting at 214°.

3-*Anilino-2-methyl-4-ketoquinazoline*,

$$C_6H_4<\begin{matrix}CO\text{———}\\N:CMe\end{matrix}>N\cdot NHPh,$$

resulting from the interaction of acetylanthranil and phenylhydrazine, forms pale yellow crystals and melts at 208—209°.

When benzoylanthranil (m. p. 122°), prepared by heating anthranilic acid with benzoyl chloride on the water-bath, interacts with the primary amines, the action ceases with the formation of the additive product.

o-Benzoylaminobenzamide, $NHBz\cdot C_6H_4\cdot CO\cdot NH_2$, produced by the action of ammonia, decomposes at 214—215°. o-*Benzoylaminobenzanilide*, $NHBz\cdot C_6H_4\cdot CO\cdot NHPh$, produced by warming benzoylanthranil with aniline, is insoluble in the ordinary organic solvents, but dissolves in hot aniline or ethyl benzoate, crystallising from the latter in slender, white needles melting at 279°. o-*Benzoylaminobenzoylphenylhydrazide*, $NHBz\cdot C_6H_4\cdot CO\cdot NH\cdot NHPh$, obtained from benzoylanthranil and phenylhydrazine, crystallises from toluene in white needles melting at 195°. G. T. M.

Action of Sulphur Chloride on Aromatic Amines. ALBERT EDINGER and JOHN B. EKELEY (*J. pr. Chem.*, 1902, [ii], 66, 209—230. Compare Abstr., 1902, i, 230).—2 : 9-*Dimethylthioquinanthren*,

$$\begin{matrix}CH:N\text{—}C\text{————}C\cdot SH\cdot C\cdot CMe:CH\cdot C\cdot CH:CH\\ CH:CH\cdot C\cdot CH:CMe\cdot C\cdot SH\cdot C\text{————}C\cdot N\text{=}CH\end{matrix},$$

formed by the action of disulphur dichloride (S_2Cl_2) on 6-methylquinoline, crystallises from glacial acetic acid in very small, almost white needles, melts at 316°, and is soluble in concentrated acids or boiling xylene. The *hydrochloride*, $C_{20}H_{16}N_2S_2,2HCl$, forms yellow needles, the *hydrobromide*, $C_{20}H_{16}N_2S_2,2HBr$, is yellow, the *picrate*,

$$C_{20}H_{16}N_2S_2,2C_6H_3O_7N_3,$$

forms yellow needles, and the *methiodide*, $C_{20}H_{16}N_2S_2,2MeI$, forms red needles.

Thioquinanthren hydrochloride, $C_{18}H_{12}N_2S_2,2HCl$, and the *hydrobromide*, $C_{18}H_{12}N_2S_2,2HBr$, form yellow needles. The base from disulphur dichloride and *o*-toluquinoline, forms a *hydrochloride*,

$$C_{18}H_{12}N_2S_2,2HCl,2H_2O,$$

which is yellow, but when anhydrous forms red needles; the *hydrobromide*, $C_{18}H_{12}N_2S_2,2HBr$, is dark red.

All the salts of the thioquinanthrens dissociate when warmed with water. With bromine in glacial acetic acid solution, the base forms unstable additive compounds.

The action of sulphur dichloride (SCl_2) on 6-methylquinoline leads to the formation of *dichloro-* and *trichloro-6-toluquinoline*. Dichloro-6-methylquinoline crystallises in colourless needles, melts at 80—81°, and forms a yellow, crystalline *picrate*, $(C_{10}H_7NCl_2)_2,H_2PtCl_6$, and a

methiodide, $C_{10}H_7NCl_2,MeI$, crystallising in reddish-yellow needles. Trichloro-6-methylquinoline crystallises in small, colourless needles, melts at 159°, and has weak basic properties.

Bromo-6-methylquinoline, formed by the action of disulphur dibromide (S_2Br_2) on 6-methylquinoline, crystallises in colourless needles, melts at 84—85°, and forms a *platinichloride*,

$$(C_{10}H_8NBr)_2,H_2PtCl_6,$$

crystallising in long, yellow needles. *Dibromo-6-methylquinoline*, formed by the action of bromine on 6-methylquinoline dissolved in fuming sulphuric acid, forms colourless needles and melts at 135—136°. The *platinichloride*, $(C_{10}H_7NBr_2)_2,H_2PtCl_6$, forms light yellow crystals. *Di-iodo-6-methylquinoline*, formed by the action of iodine on 6-methylquinoline dissolved in fuming sulphuric acid, crystallises in colourless, glistening needles, melts at 135—136°, and forms a *platinichloride*, $(C_{10}H_7NI_2)_2,H_2PtCl_6$.

When heated with fuming nitric acid, di-iodo-*p*-toluquinoline forms *iodonitro-6-methylquinoline*, $C_{10}H_7NI\cdot NO_2$, which crystallises in light yellow needles and melts at 133°.

Contrary to previous statements (*loc. cit.*), acetyl derivatives of the thioquinanthren bases are not formed by the action of acetyl chloride.

G. Y.

Action of Acetic Anhydride on Osazones: Formation of Osotriazoles. Heinrich Biltz and Rudolf Weiss (*Ber.*, 1902, **35**, 3519—3524).—The formation of triphenylosotriazole as a bye-product in the acetylation of benzil-β-osazone has been previously described (Abstr., 1899, i, 502); it forms, however, the sole product if the osazone is heated with three times its weight of acetic anhydride at 135° for seven or eight hours in a sealed tube. Triphenylosotriazole readily forms a *tribromo*-derivative, which crystallises in small, white needles and melts at 193—194°, a p-*nitro*-derivative, which crystallises in pale yellow needles or rhombohedra and melts at 160—162°, and a *trinitro*-derivative, which crystallises in slender needles and melts at 285—286°.

Benzil-p-*nitrophenylhydrazone* crystallises in flat prisms of a dark orange colour, melts at 192—193°, and, like benzil-*p*-nitro-osazone (Abstr., 1899, i, 689), dissolves in alcoholic potash, giving a reddish-violet solution. Benzil-*p*-nitro-osazone, when boiled with acetic anhydride and sodium acetate, yields a mixture of the nitrotriphenylosotriazole just described and the *diacetyl* derivative of the osazone, which crystallises in small, flat needles and melts at 244°.

The acetylation of salicyl-α-osazone (compare *loc. cit.*) yields a mixture of the *tetra-acetyl* derivatives of salicyl-α-osazone and salicyl-β-osazone melting at 228° and 194—195° respectively. R. H. P.

B-**Dimethylnaphthasafranine.** Otto Fischer and Eduard Hepp (*Zeit. Farb. Text. Chem.*, 1902, **1**, 437—439).—*B-Dimethylnaphthasafranine*, $NMe_2\cdot C_6H_3<\begin{matrix}N{=\!=}C{-\!-\!-}C_6H_4\\ NPh{:}C\cdot CH\cdot C\cdot NH\end{matrix}$, is a bye-product of the action of nitrosodimethylaniline on α-naphthylamine hydrochloride

in the presence of aniline (compare Abstr., 1893, i, 333; 1895, i, 608); it crystallises from benzene in prisms having a metallic lustre, and containing 1 mol. of the solvent. The *hydrochloride* separates from alcohol in acicular prisms having a green reflex; the *nitrate* and the *hydrobromide* are obtained in green needles and leaflets respectively; the freshly precipitated *hydriodide* is amorphous, and slowly takes the form of green needles. The *mercurichloride*, *platinichloride*, and *aurichloride* also separate in green, acicular crystals.

When heated with a mixture of concentrated acetic and hydrochloric acids, the base becomes converted into the corresponding hydroxyrosindone (naphthasafranol); this compound is also obtained by the action of alcoholic potassium hydroxide on the base at 140—150°, but in this case dimethylnaphthasafraninone is simultaneously produced.

When heated at 160—170° with a mixture of *p*-phenylenediamine, *p*-phenylenediamine hydrochloride, and alcohol, dimethylnaphthasafranine yields p-*aminophenyl-B-dimethylnaphthasafranine*,

$$NMe_2\cdot C_6H_3 < \begin{matrix} N{=\!=}C\text{——}C_6H_4 \\ NPh{:}C\cdot CH{:}C\cdot N\cdot C_6H_4\cdot NH_2 \end{matrix} ;$$

this product crystallises from alcohol in dark brown needles and furnishes salts with the mineral acids which separate out from the same solvent as crystalline precipitates with a bronze reflex.

The constitution of the preceding base is indicated by the result of its decomposition by concentrated hydrochloric acid at 180—200°, the products being hydroxyrosindone, *p*-phenylenediamine, dimethylnaphthasafraninone, and tarry substances which yield quinone on oxidation with ferric chloride. *B*-Dimethylnaphthasafranine is readily diazotisable either in aqueous or in alcoholic solution.

The prefix "*B*," employed in designating these safranine derivatives, indicates that the substituent is in the benzene nucleus.

G. T. M.

Civet. ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1902, **27**, [iii], 997—1000).—The three samples examined varied in colour from yellowish-brown to brown; they were of soft consistence and possessed stercoraceous odours which became less unpleasant in small quantities. The specimens melted somewhat indefinitely at 36—37° and were readily soluble in organic solvents with the exception of alcohol and acetone, leaving a residue of hair, &c., forming from 3·6—5·3 per cent. of the whole; these solutions were not optically active. The ash in the samples varied from 0·6—1·2 per cent. When treated with alcoholic potash, they furnished from 51—70 per cent. of solid fatty acids. Two of the samples, when steam distilled, readily gave a distillate containing scatole, but the third did not (compare Wahlbaum, Abstr., 1900, i, 509). T. A. H.

Organic Chemistry.

Products of the Slow Combustion of *iso*Pentane, *n* Hexane, and *iso*Butyl Alcohol. Richard von Stepski (*Monatsh.*, 1902, 23, 773—801).—A stream of air saturated with the vapour was passed slowly over glowing platinum, and the products of combustion were passed through a condenser cooled to $-15°$, and any uncondensed gas led into bromine; the bromides thus formed were separated by repeated fractional distillation under 15 mm. pressure.

*iso*Pentane gave formaldehyde, ethylene, propylene, $\Delta^{\alpha\beta}$- and $\Delta^{\beta\gamma}$-butylenes, *iso*butylene, two *iso*amylenes, butadiene (?), water, and carbon dioxide, only the first two mentioned being formed in quantity. Similarly, *n*-hexane gave formaldehyde, ethylene, propylene, $\Delta^{\alpha\beta}$- and $\Delta^{\beta\gamma}$-butylenes, two amylenes, three hexylenes, butadiene (?), water, and carbon dioxide. Equations are given to explain the formation of these products.

*iso*Butyl alcohol gave *iso*butaldehyde, *iso*butyric acid, formaldehyde, ethylene, propylene, *iso*butylene, water, and an acetal (?) (compare Trillat, Abstr., 1901, i, 444, 496). E. F. A.

Preparation of Iodoform by means of Acetylene. Octave Le Comte (*J. Pharm. Chim.*, 1902, [vi], 16, 297—300).—Acetylene mercuric chloride, silver and cuprous acetylides, and a solution of acetylene in concentrated sulphuric acid all yield iodoform when treated with iodine and dilute sodium hydroxide solution. G. D. L.

Formula of Trimethylethylene Nitrosite. Arthur Hantzsch (*Ber.*, 1902, 38, 4120—4121).—A reply to Schmidt (this vol., i, 2). T. M. L.

Condensation of Ethyl Alcohol with Heptyl Alcohol. Formation of Normal Nonyl Alcohol. Marcel Guerbet (*Bull. Soc. chim.*, 1902, [iii], 27, 1034—1036).—When sodium (30 parts) is dissolved in a mixture of heptyl alcohol (300 parts) and ethyl alcohol (250 parts), and the solution heated in closed vessels at 230°, there is produced *n*-nonyl alcohol (8 parts) and a tetradecyl alcohol (1 part). T. A. H.

Condensation of Heptyl Alcohol with Propyl Alcohol. Formation of β-Methylnonyl Alcohol. Marcel Guerbet (*Bull. Soc. chim.*, 1902, [iii], 27, 1036—1038).—When a mixture of 100 grams of heptyl alcohol with 250 grams of propyl alcohol is treated as described in the preceding abstract, 18 grams of β-methylnonyl alcohol and a small quantity of a hexyl alcohol are formed. *β-Methylnonyl alcohol*, $CH_3\cdot[CH_2]_6\cdot CHMe\cdot CH_2\cdot OH$, is a colourless, oily liquid which boils at 221—223° (corr.) and has a sp. gr. 0·8457 at 0° and 0·8333 at 15°. The *acetate* has a faint lemon-like odour, boils at 238—240°, and has

a sp. gr. 0·8812 at 0° and 0·8705 at 15°. *α-Methylnonoic acid*, $CH_3\cdot[CH_2]_6\cdot CHMe\cdot CO_2H$, obtained by the action of potassium hydroxide on the alcohol, is a colourless oil with the odour of perspiration; it boils at 261—265° (corr.) and furnishes an *amide* crystallising in prismatic needles which melt at 76°. When oxidised with chromic acid, it forms methyl heptyl ketone, octoic, heptoic, and acetic acids, and carbon dioxide, whence the formulæ assigned to the acid and alcohol. When two alcohols are condensed in this way, the oxygen of the molecule of water eliminated is furnished by the higher alcohol.

T. A. H.

Presence of Volemitol in some Primulaceæ. J. Bougault and G. Allard (*Compt. rend.*, 1902, **135**, 796—797).—The polyhydric alcohol, extracted by 85 per cent. alcohol from the roots of *Primula grandiflora* and previously described as primulitol, is now recognised as volemitol, $C_7H_{16}O_7$, discovered by Bourquelot (Abstr., 1895, i, 273). Volemitol has been further purified, and the following constants have been obtained. It melts at 154—155°; in aqueous solution, it has $[\alpha]_D$ +2·65°, this being independent of the concentration and not affected by boric acid, although sodium borate increases it. Its ethyl acetal melts at 206° and has $[\alpha]_D$ −46·4° in chloroform solution. Its acetate melts at 62°.

It is contained in *Primula elatior* and *Primula officinalis*, and in a large variety of *Primulæ*. The proportion contained in all these different species is about the same, namely, 1·5 per cent. of the dry plant.

J. McC.

Solid Acid from the Oil of Elæococca Vernicia. Léon Maquenne (*Compt. rend.*, 1902, **135**, 696—698.)—Cloez (*Compt. rend.*, 1875, **81**, 469; 1876, **82**, 501, and **83**, 943) isolated from the oil of *Elæococca vernicia* an acid (m. p. 48°) to which he gave the name elæomargaric acid, $C_{16}H_{29}\cdot CO_2H$; it was very readily converted, by dissolving in carbon disulphide, into an acid (m. p. 71°) of the same composition which he took to be a polymeride, and called elæostearic acid. On reinvestigation, it was found that the two acids had the same mol. weight, and further that the acid melting at 48° was converted into the acid melting at 71° by the action of traces of sulphur or iodine. The two acids are therefore probably stereoisomeric, and it is suggested that they should be called α- and *β-elæostearic acid* respectively. Owing to the great rapidity with which the acids absorb oxygen, it was extremely difficult to get trustworthy analyses. The numbers given by the purest material point to the formula $C_{17}H_{29}\cdot CO_2H$, the acids being therefore isomeric with linolenic acid. Oxidation of both acids with permanganate produced azelaic acid (m. p. 105—106°) and valeric acid. K. J. P. O.

The Supposed Separation of the Two Desmotropic Forms of Ethyl Acetoacetate. Paul Rabe (*Ber.*, 1902, **35**, 3947—3952. Compare Schiff, Abstr., 1898, i, 237, and *Ber.*, 1899, **32**, 86).—From a purely theoretical standpoint, Schiff's results are untenable.

Most of Schiff's experiments have been repeated, but the results are not confirmed. The products obtained under the varying conditions appear to be mixtures and the melting points vary considerably. All the preparations exhibit the same reaction towards ferric chloride, all appear to be unimolecular, and the ebullioscopic method in benzene solution gives low numbers showing that decomposition undoubtedly occurs, followed, as the solution cools, by recombination.

J. J. S.

Action of Aliphatic Acid Chlorides on the Sodium Derivatives of Acetoacetic Esters. Louis Bouveault and A. Bongert (*Bull. Soc. chim.*, 1902, [iii], 27, 1038—1046).—An historical summary of previous work on the preparation of *O*-acyl and *C*-acyl derivatives of acetoacetic ester is given. A mixture of the two isomerides is produced when an acid chloride is added drop by drop to the sodium derivative of an acetoacetic ester suspended in ether. When the acid chloride is of low molecular weight, the isomerides so produced can be separated by a method already described (Bouveault, Abstr., 1900, i, 474), but for acid chlorides of higher mol. weight the residue obtained after distilling off the solvent is washed with 8 per cent. sodium hydroxide solution, which dissolves out the *C*-acyl isomeride and regenerates the latter on acidification; this is purified by shaking with sodium carbonate to remove fatty acids, and fractionation to remove unattacked ester.

T. A. H.

***C*-Acyl Derivatives of Acetoacetic Esters.** Louis Bouveault and A. Bongert (*Bull. Soc. chim.*, 1902, [iii], 27, 1046—1049. Compare Abstr., 1901, i, 311).—The following esters have been prepared by the methods described in the preceding abstract. They are all colourless liquids which boil without decomposition under reduced pressure, have slight odours, and give red colorations with ferric chloride. With sodium ethoxide in alcohol, they form soluble, crystalline sodium derivatives, and with aqueous copper acetate well-crystallised copper compounds.

Methyl C-*isovalerylacetoacetate*, $C_4H_9 \cdot CO \cdot CHAc \cdot CO_2Me$, boils at 107—108° under 11 mm. pressure and has a sp. gr. 1·069 at 0°/4°. The *copper* derivative forms blue needles, melts at 137°, and is insoluble in petroleum or ether.

Methyl C-*hexoylacetoacetate*, $C_5H_{11} \cdot CO \cdot CHAc \cdot CO_2Me$, boils at 140° under 22 mm. pressure and has a sp. gr. 1·056 at 0°/4°. The *copper* derivative forms blue needles, melts at 92°, and dissolves easily in organic solvents with the exception of light petroleum.

Ethyl C-*propionylacetoacetate*, $CEtO \cdot CHAc \cdot CO_2Et$, boils at 111° under 20 mm. pressure and has a sp. gr. 1·091 at 0°/4°; the *copper* derivative crystallises in blue needles melting at 80° and is easily soluble in most organic solvents, but less so in light petroleum.

Ethyl C-*butyrylacetoacetate*, $CPr^{\alpha}O \cdot CHAc \cdot CO_2Et$, boils at 112° under 16 mm. pressure and has a sp. gr. 1·062 at 0°/4°. The *copper* derivative forms slender, blue needles melting at 92°.

Ethyl C-*isobutyrylacetoacetate*, $CPr^{\beta}O \cdot CHAc \cdot CO_2Et$, boils at 114° under 15 mm. pressure and has a sp. gr. 1·061 at 0°/4°.

Ethyl C-iso*valerylacetoacetate*, $C_4H_9\cdot CO\cdot CHAc\cdot CO_2Et$, boils at 118° under 12 mm. pressure and has a sp. gr. 1·043 at 0°/4°. The *copper* derivative forms small, light blue crystals melting at 110°.

Ethyl C-*hexoylacetoacetate*, $C_5H_{11}\cdot CO\cdot CHAc\cdot CO_2Et$, boils at 136° under 10 mm. pressure and has a sp. gr. 1·032 at 0°/4°. The *copper* derivative separates from methyl alcohol in violet-blue needles and melts at 53°. T. A. H.

O-**Acyl Derivatives of Acetoacetic Esters.** LOUIS BOUVEAULT and A. BONGERT (*Bull. Soc. chim.*, 1902, [iii], **27**, 1050—1055. Compare Abstr., 1901, i, 311).—These substances are acyl derivatives of β-hydroxycrotonic esters and are obtained as described in the two preceding abstracts; they are colourless, slightly odorous liquids, which distil without decomposition under reduced pressure, have slightly higher specific gravities than the isomeric *C*-acyl derivatives, and unlike these give no colour reaction with ferric chloride.

Methyl β-iso*valeryloxycrotonate*, $C_4H_9\cdot CO\cdot O\cdot CMe\dot{:}CH\cdot CO_2Me$, boils at 113—114° and has a sp. gr. 1·039 at 0°/4°.

Methyl β-hexoyloxycrotonate, $C_5H_{11}\cdot CO\cdot O\cdot CMe\dot{:}CH\cdot CO_2Me$, becomes brown when exposed to air and light; it boils at 132° under 12 mm. pressure.

Ethyl β-propionyloxycrotonate, $COEt\cdot O\cdot CMe\dot{:}CH\cdot CO_2Et$, boils at 106° under 12 mm. pressure, has a sp. gr. 1·061 at 0°/4°, and becomes slightly yellow when kept.

Ethyl β-butyryloxycrotonate, $COPr^{\alpha}\cdot O\cdot CMe\dot{:}CH\cdot CO_2Et$, boils at 111—112° under 10 mm. pressure and has a sp. gr. 1·033 at 0°/4°.

Ethyl β-iso*butyryloxycrotonate*, $COPr^{\beta}\cdot O\cdot CMe\dot{:}CH\cdot CO_2Et$, boils at 117° under 15 mm. pressure and has a sp. gr. 1·033 at 0°/4°.

Ethyl β-iso*valeryloxycrotonate*, $C_4H_9\cdot CO\cdot O\cdot CMe\dot{:}CH\cdot CO_2Et$, boils at 122° under 14 mm. pressure and has a sp. gr. 1·018 at 0°/4°.

Aqueous ammonia converts methyl β-butyryloxycrotonate into ammonium butyrate and methyl acetoacetate, whilst gaseous ammonia passed into an ethereal solution of the ester furnishes butyramide and methyl β-aminocrotonate (compare Abstr., 1901, i, 311).

Phenylhydrazine reacts with methyl β-butyryloxycrotonate dissolved in ether, producing butyrylphenylhydrazine, phenylmethylpyrazolone, and a small quantity of *bis*-phenylmethylpyrazolone.

Hydrazine reacts similarly, forming methylpyrazolone and *butyrylhydrazine*, $COPr\cdot NH\cdot NH_2$. This crystallises in deliquescent, colourless needles, is soluble in all ordinary solvents except light petroleum, boils at 120° under 10 mm. pressure, and reduces Fehling's solution. It reacts with benzaldehyde to form the corresponding *hydrazone*, which crystallises in long needles, melts at 97°, and is soluble in ether, alcohol, and chloroform, but insoluble in light petroleum and water. *Acetone butyrylhydrazone*, $COPr\cdot NH\cdot N\dot{:}CMe_2$, obtained by the solution of butyrylhydrazine in acetone, forms colourless crystals melting at 83° and readily soluble in acetone, ether, alcohol, and water, but almost insoluble in light petroleum. T. A. H.

Camphocarboxylic Acid. III and IV. JULIUS W. BRÜHL (*Ber.*, 1902, **35**, 4030—4040; 4113—4119. Compare this vol., i, 4). —*Methyl acetylcamphocarboxylate*, prepared by the action of acetyl

chloride on the sodium derivative, is a colourless, odourless, viscous oil, boils at 142° under 12 mm. pressure, is insoluble in dilute alkali hydroxides, but readily soluble in organic solvents; it does not decolorise bromine or permanganate but is readily hydrolysed by alkalis or acids to acetic and camphocarboxylic acids, and is therefore regarded as the acetate of an enolic modification, $C_8H_{14}<\begin{matrix}C\cdot CO_2Me\\ \| \\ C\cdot OAc\end{matrix}$, a conclusion which is in accordance with the optical properties of the substance.

The sodium derivative of amyl camphocarboxylate is soluble in ether, benzene, or light petroleum. *Amyl acetylcamphocarboxylate* is a thick, colourless, odourless oil and boils at 170—171° under 10·5 mm. pressure; its properties are similar to those of the methyl ester and it is therefore also regarded as an enolic acetate,

$$C_8H_{14}<\begin{matrix}C\cdot CO_2\cdot C_5H_{11}\\ \| \\ C\cdot OAc\end{matrix}.$$

Amyl camphocarboxylate is not acted on by acetyl chloride in pyridine solution, and the corresponding ketonic acetate has not yet been prepared.

Ethyl iso*valerylcamphocarboxylate* is a viscous, colourless oil and boils at 174—176° under 13 mm. pressure; the optical properties are in accord with the formula $C_8H_{14}<\begin{matrix}C\cdot CO_2Et\\ \| \\ C\cdot O\cdot CO\cdot C_4H_9\end{matrix}$, and agree exceedingly closely with those of the isomeric amyl acetylcamphocarboxylate; the ester is readily hydrolysed to ethyl alcohol, camphocarboxylic acid, and *iso*valeric acid by alkalis, by hydrochloric acid, and even by dilute acetic acid.

Ethyl benzoylcamphocarboxylate crystallises from 90 per cent. alcohol in beautiful, long, rhombic prisms, melts at 46—47°, boils at 218—218·5° under 14 mm. pressure, is readily hydrolysed by methyl alcoholic potassium hydroxide, but much less readily by hydrochloric acid; no trace of benzoylcamphor is formed in the hydrolysis, and the product therefore consists entirely of the enolic benzoate,

$$C_8H_{14}<\begin{matrix}C\cdot CO_2Et\\ \| \\ C\cdot OBz\end{matrix}.$$

The products of interaction of methyl sodium camphocarboxylate and benzenesulphonic chloride are benzenesulphinic acid and (under varying conditions) two methyl chlorocamphocarboxylates, which are probably stereoisomerides of the formula $C_8H_{14}<\begin{matrix}CCl\cdot CO_2Me\\ | \\ CO\end{matrix}$.

Methyl chlorocamphocarboxylate separates from 60 per cent. alcohol in tablets and melts at 53—54°. *Methyl* iso*chlorocamphocarboxylate* separates in prismatic crystals and melts at 60—61°. *Amyl chlorocamphocarboxylate*, prepared by a similar method from amyl sodium-camphocarboxylate and benzenesulphonic chloride, is an oil boiling at 182—183° under 12 mm. pressure and is perhaps a mixture of stereoisomerides.

Methyl chlorocamphocarboxylate, like the methyl alkylcamphocarboxylate, cannot be hydrolysed by mineral acids, but is very readily hydrolysed by methyl alcoholic sodium or potassium hydroxide. The hydrolysis does not proceed in any simple manner; α-chlorocamphor

is formed, and a small amount of an acid was isolated which melted at 116—117°, and which may perhaps be a stable α'-chlorocampho-α-carboxylic acid. T. M. L.

Oxalomolybdites. G. Bailhache (*Compt. rend.*, 1902, **135**, 862—865. Compare Abstr., 1901, ii, 243).—A *potassium oxalomolybdite*, $MoO(OH)_3,C_2O_4HK$, is prepared by dissolving molybdenum sulphate, $Mo_2O_5,2SO_3$ (1 mol.), and oxalic acid (2 mols.) in water, exactly precipitating the sulphuric acid with barium hydroxide, adding the necessary quantity of potassium carbonate, and concentrating in a current of carbon dioxide. The salt forms orange-red, hydrated crystals, which become yellow on losing water. On treatment with an ammonium chloride solution saturated with hydrogen chloride, the compound $MoOCl_3,2NH_4Cl$ is obtained in grass-green crystals. By nitric acid, the potassium salt is converted into an oxalomolybdate. When heated at 115—180°, it decomposes according to the equation

$$2MoO(OH)_3,C_2O_4HK = MoO_2 + K_2MoO_4 + 2CO + 2CO_2 + 4H_2O.$$

Ammonium oxalomolybdite forms orange-red crystals, with H_2O, which lose water and become yellow in a desiccator. The *barium* salt separates in red crystals, with H_2O, and is very insoluble. It is also formed by treating the green ammonium chloride compound just mentioned with oxalic acid and barium chloride. K. J. P. O.

Microscopic Examination of [Succinates of] the Rare Earths. Richard J. Meyer (*Zeit. anorg. Chem.*, 1902, **33**, 31—44).—The microscopic appearance of the succinates of the metals of the cerite group has been examined. The form depends on the concentration of the solution. Neodymium and praseodymium succinates separate from dilute solution in small needles, and from more concentrated solution in starry aggregates. Samarium succinate separates in precisely the same form. Lanthanum succinate also separates in this form as well as in rhomboids.

From all the cerium preparations, cerium succinate separates in rhomboids resembling those of lanthanum succinate as well as in needles; whether this is due to the actual presence of lanthanum or whether this form is also characteristic of cerium succinate is doubtful.

From an exhaustive examination of these succinates, the author believes that the microscopic method is insufficient for deciding as to the homogeneity of cerite earth preparations. J. McC.

Synthesis of Alkylated Glutaric Acids from β-Glycols. I. Synthesis of α-Methylglutaric Acid. Adolf Franke and Moriz Kohn (*Monatsh.*, 1902, **23**, 740—746).—*α-Methyltrimethylene dicyanide* [*$\alpha\gamma$-dicyanobutane*], prepared from the bromide of β-butylene glycol and potassium cyanide, is a colourless liquid, which boils at 269—271° under atmospheric pressure, and at 134° under 13 mm.; it is easily soluble in water, alcohol, or ether. On hydrolysis with acids, it is converted into α-methylglutaric acid. E. F. A.

Selenodilactylic Acids. Nils Coos (*Ber.*, 1902, **35**, 4109—4112).—Two stereoisomeric *selenodilactylic acids*, $Se(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$, are obtained in the form of potassium salts by the action of potassium

α-bromopropionate on hydrogen selenide dissolved in aqueous potassium hydroxide. The acid, which is the principal product, crystallises from water in monoclinic prisms, [$a:b:c = 1.0089:1:1.3345$; $\beta = 114°32'$], melts at 145°, and has μ_{∞} 356, K 0.0116; from the mother liquors of this acid, a rhombic form, [$a:b:c = 0.9210:1:1.2360$], is obtained which melts at 106—107° and has $K = 0.0380$. The sodium and potassium salts are very easily soluble; the *barium* salts each exist in two forms, as in the case of the analogous thio-acids, one amorphous and easily soluble, the other crystalline and sparingly soluble. The *amide* of the monoclinic acid crystallises in long needles, that of the rhombic acid in plates. W. A. D.

Metacetaldehyde. WALTHER BURSTYN (*Monatsh.*, 1902, 23, 731—739).—A determination of some physical constants. The vapour tension rises regularly with the temperature up to 80°, when decomposition begins. The vapour density, determined by Hofmann's method, was found to vary between 25.5 and 26.6. The numbers obtained for the molecular weight, as determined by the freezing point method, increase with the concentration, but fall between those required for $3C_2H_4O$ and $4C_2H_4O$, and as the partial dissociation into acetaldehyde must lead to too low a result, the quadrimolecular formula, $C_8H_{16}O_4$, is probably indicated. E. F. A.

Action of Sodium Dioxide on Paraformaldehyde. LUDWIG VANINO (*Zeit. anal. Chem.*, 1902, 41, 619—620).—Solid sodium peroxide thrown into formaldehyde solution generally produces detonation. Solid paraformaldehyde brought into contact with dry sodium peroxide is instantly inflamed. M. J. S.

Synthesis of Organic Acids, Carbohydrates, and Proteids JULIUS WALTHER (*Chem. Zeit.*, 1902, 26, 1001—1002).—The author describes the apparatus used in his synthetical experiments (compare Abstr., 1902, i, 747). K. J. P. O.

Oxidation Products of Rhodeose. EMIL VOTOČEK (*Zeit. Zuckerind. Böhm.*, 1902, 27, 15—27. Compare Abstr., 1900, i, 332, and 1901, i, 368).—In order to discover the cause of the difference in specific rotations between syrupy rhodeose ($[\alpha]_D + 36°$) and the crystalline sugar ($[\alpha]_D + 75.2$) (*loc. cit.*), the author has studied the products of oxidation of the syrupy modification by means of bromine in presence of water. From the resulting mixture of acids, two barium salts were separated.

(1) *Barium rhodeonate*, $(C_6H_{11}O_6)_2Ba$, is sparingly soluble in water and crystallises with either 1 or $2H_2O$; free rhodeonic acid was not obtained, as it passes readily into *rhodeolactone*, which melts at 105.5°, is readily soluble in water, and has $[\alpha]_D - 76.3°$; reduction of the lactone by means of dilute sulphuric acid and sodium amalgam yields rhodeose. From dilute alcohol, *potassium rhodeonate* crystallises, with $1\frac{1}{2}H_2O$, in thin, colourless prisms soluble in water.

(2) *Barium* iso*rhodeonate*, which is isomeric with, and more soluble

in water than, the rhodeonate, separates, with $2H_2O$, as a microcrystalline mass. iso*Rhodeonic acid*, which was obtained as a yellowish-brown syrup, gives a value $+16°$ for $[\alpha]_D$, and is much less readily converted into a lactone than rhodeonic acid; oxidation of the acid by means of nitric acid gives rise to trihydroxyglutaric acid, showing that the corresponding sugar, *iso*rhodeose, is a methylpentose; the *potassium* salt was prepared and analysed. Reduction of a mixture of *iso*rhodeonic acid and its lactone, by means of sodium amalgam in presence of water, yields a sugar to which the name iso*rhodeose* is given, and which strongly reduces Fehling's solution, has a lower specific rotation than rhodeose, and yields a *phenylosazone* crystallising in short, yellow, prism-like needles melting at 189—190°. With hydrazine or substituted hydrazines, *iso*rhodeose does not form insoluble hydrazones.

The author compares the properties of rhodeose with those of fucose (see Tollens, Abstr., 1890, 1393), which is probably the optical antipode of rhodeose. T. H. P.

Action of Formaldehyde on Starch: Iodo-compound of Amylodextrin. VICTOR SYNIEWSKI (*Annalen*, 1902, **324**, 201—212; *Bull. Acad. Sci. Cracow*, 1902, 435—441).—Potato starch, when mixed with 40 per cent. formaldehyde solution, is not immediately attacked, but after three days its granules commence to coagulate, their circumferential parts vitrify, and only the unaltered interiors give the iodine reaction. This alteration increases until the mixture becomes gelatinous and homogeneous, and, on adding a further quantity of the aldehyde solution, the product becomes mobile, and after two months acquires the consistence of an ordinary starch solution of similar concentration, but does not give the coloration with iodine. The condensation product, which is not identical with Claassen's amyloform (*Chem. Centr.*, 1879, i, 160), is readily decomposed on heating, and is slowly hydrolysed by water and rapidly by acids, giving rise to a substance closely resembling amylodextrin; this substance rapidly recombines with the aldehyde to give the original compound.

These results indicate that a concentrated formaldehyde solution hydrolyses starch, giving rise to a substance of the carbinol type which does not reduce Fehling's solution and which interacts with the aldehyde, yielding a readily hydrolysable condensation product. The latter process is employed in purifying amylodextrin, this substance dissolving in formaldehyde solution, whilst its impurities remain insoluble; the filtrate, on evaporation, yields microscopic granules composed of concentrically arranged layers of small needles, and, under polarised light, these aggregates exhibit a well-defined, black cross.

The iodine derivative of amylodextrin, prepared by hydrolysing the formaldehyde compound with dilute acid and adding a standard potassium iodide solution of iodine, is precipitated by the addition of a saturated sodium chloride solution, and its composition is determined by titrating the residual iodine. In this way, the formula

$$[C_{54}H_{90}O_{45},\tfrac{3}{2}(H_2O)I_3]_4$$

is obtained.

Formaldehydeamylodextrin, which does not react with iodine, probably contains the aldehyde combined in some way with its primary alcoholic radicles $\cdot CH_2\cdot OH$. The progress of hydrolysis is indicated by the colour reaction with iodine; when one of these groups is present, a brown colour is observed; a red coloration is obtained when two of these react, and the blue iodoamylodextrin results when three alcoholic residues participate in the interaction. G. T. M.

Constitution of Starch. VICTOR SYNIEWSKI (*Annalen*, 1902, **324**, 212—268; *Bull. Acad. Sci. Cracow*, 1902, 411—454. Compare Abstr., 1900, i, 78).—A starch emulsion of known strength, containing a small amount of formaldehyde, is treated with malt extract prepared at 76—78°, and samples taken out from time to time are tested by Fehling's solution. The results indicate that hydrolysis takes place rapidly until the mixture contains 30·72 per cent. of maltose, but from this stage onwards the reaction proceeds very slowly. The critical point at which the rate of hydrolysis changes corresponds with the stage at which the mixture ceases to give any characteristic coloration with iodine solution. With a starch solution containing 0·021286 gram of amylogen per c.c., this change occurs after 216 hours, and when this solution is treated with fresh malt extract prepared at the ordinary temperature, hydrolysis takes place much more rapidly, until after 48 hours the percentage of maltose has risen to 92·36, then the reaction slackens again considerably, so that after 96 hours the percentage of the sugar is only 93·05. Similar results are obtained by adding the cold malt extract at other stages in the hydrolysis of starch by the heated extract. The dextrin which remains when the action of the cold extract begins to slacken is called *protodextrin* I ("*Grenzdextrin I*") and that which resists the action of the heated extract is designated *protodextrin* II ("*Grenzdextrin II*.") The latter is isolated by adding the partially hydrolysed solution to boiling water, evaporating, filtering, and precipitating with 90 per cent. alcohol; it is finally extracted with methyl alcohol to remove the last traces of sugar.

Protodextrin II, $C_{36}H_{62}O_{31}$, a pale yellow powder with a sweet taste, is moderately soluble in dilute alcohol, the solubility diminishing as the concentration of the alcohol increases; it has $[\alpha]_D$ +179 36′ at 20°, its molecular weight, as determined by the cryoscopic method in aqueous solution, is 1039.

This dextrin, which is readily hydrolysed by cold malt extract, is apparently identical with α-maltodextrin (Ling and Baker, Trans., 1897, 71, 517), achroodextrin II (Lintner and Düll, Abstr., 1895, i, 409), and maltodextrin (Brown and Morris, Trans., 1885, **47**, 527).

When a 3 per cent. solution of protodextrin II is treated for 1 hour with fresh malt extract, 60 per cent. is converted into sugar (maltose), and a substance having the composition $C_{21}H_{42}O_{21}$ is precipitated on adding alcohol; this product, to which the name γ-*maltodextrin* is given, resembles protodextrin II, and is readily soluble in dilute alcohol, dissolving, however, more sparingly in the concentrated solvent; it has $[\alpha]_D$ +172°17′ at 20°; its molecular weight, determined by the cryoscopic method in aqueous solution, is 595. The

hydrolysis of γ-maltodextrin by fresh cold malt extract takes place at first very rapidly until 94·06 per cent. has been converted into sugar.

γ-Maltodextrin is undoubtedly identical with Ling and Baker's β-maltodextrin (Trans., 1897, **71**, 518) and with Prior's achroodextrin III (Abstr., 1897, i, 312).

The formation of this substance from protodextrin II takes place in accordance with the following equation: $C_{36}H_{62}O_{31} + H_2O = C_{24}H_{42}O_{21} + C_{12}H_{22}O_{11}$. *iso*Maltose is extracted by alcohol from the residue obtained by evaporating down the product of the action of fresh malt extract on γ-maltodextrin; the osazone obtained from this sugar has the characteristics of Lintner's *iso*maltosazone, and is not contaminated with dextrinous substances as suggested by Brown and Millar (Trans., 1899, **75**, 292. Compare also Ling and Baker, Trans., 1895, **67**, 739).

Protodextrin II yields, on hydrolysis, 2 mols. of maltose to 1 of *iso*maltose, whilst γ-maltodextrin gives rise to equal mols. of the two sugars.

Protodextrin I (Lintner's achroodextrin I), $C_{72}H_{124}O_{62}$, is a white powder, very slowly hydrolysed by freshly prepared cold malt extract in the presence of formaldehyde, yielding a mixture of dextrose, maltose, and *iso*maltose; the first two sugars are removed by extracting the syrupy product of evaporation with hot dilute alcohol, the *iso*maltose and dextrinous substances remain undissolved, the biose being then dissolved out by 90 per cent. alcohol. The *iso*maltose, which is purified by crystallisation from a mixture of methyl and ethyl alcohols, decomposes at 82—85° and has $[\alpha]_D$ +141°40′ at 20°; its osazone melts sharply at 152—153°. This sugar is not identical with Fischer's *iso*maltose and is accordingly designated *dextrinose*.

Amylodextrin, the product obtained by heating a 5 per cent. starch emulsion at 140°, has a composition corresponding with

$$(C_{54}H_{90}O_{45})_n, \tfrac{3}{2}nH_2O \text{ or } (C_{54}H_{96}O_{48})_n, -\tfrac{3}{2}nH_2O.$$

This molecule contains 93 hydrogen atoms, of which only 30 can be hydroxylic. The *acetyl* derivative of amylodextrin, obtained by the action of acetic anhydride, is a white, amorphous powder decomposing at 280—281°; its composition corresponds with the formula $n[(C_{54}H_{66}O_{48} - \tfrac{3}{2}H_2O)(C_2H_3O)_{30}]$. From this compound, the amylodextrin is regenerated by the action of sodium hydroxide solution.

A 10 per cent. starch paste, when heated under pressure and allowed to evaporate, deposits a precipitate containing amylodextrin and a reversion product of this substance. The mixture is dehydrated in alcohol, and, after drying, is extracted with hot water, which removes the amylodextrin, leaving its reversion product; the latter substance has the composition corresponding with $(C_{54}H_{90}O_{45})_n + nH_2O$, and is therefore formed from amylodextrin by the abstraction of water.

The rate of hydrolysis of this substance with fresh malt extract is intermediate between those of starch and amylodextrin.

The amylogen residue of the starch molecule, which contains three

maltose residues, loses these by hydrolysis with malt extract when a preliminary carbinol hydrolysis has led to the addition of hydroxyl groups, this operation taking place in three stages.

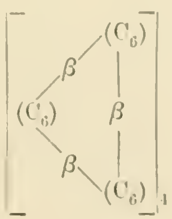
These experimental results are discussed at considerable length and the salient points of the theoretical part are summarised in the following manner.

The nine dextrose residues of which the amylogen radicle is composed are linked together by nine monocarbonyl linkings. Three of these, the α-linkings, connect the protodextrin I residue with three maltose residues. Three other linkings, indicated by the letter β, join together the three dextrose residues which make up the protodextrin I complex, and the last three, γ-linkings, connect the pairs of dextrose residues which make up the three maltose residues. The amylogen complex is accordingly thus represented:

$$\begin{array}{ll} & (C_6)\cdot\alpha\cdot(C_6)\cdot\gamma\cdot(C_6) \\ & \;\diagdown\beta \\ \beta & (C_6)\cdot\alpha\cdot(C_6)\cdot\gamma\cdot(C_6) \\ & \;\diagup\beta \\ & (C_6)\cdot\alpha\cdot(C_6)\cdot\gamma\cdot(C_6) \end{array} .$$

The decomposition of the amylogen residue by fresh malt extract results from the rupture of the α-linkings; the hydrolysis induced by the heated extract leads to the disruption of the β-linkings.

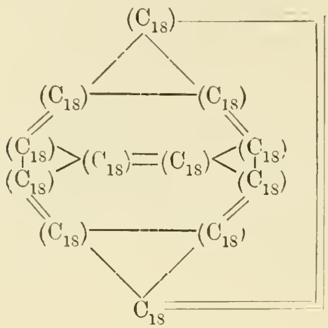
Protodextrin II is accordingly represented by the formula $(C_6)\cdot\gamma\cdot(C_6)\cdot\alpha\cdot(C_6)\cdot(C_6)\cdot\alpha\cdot(C_6)\cdot\gamma\cdot(C_6)$, and this is hydrolysed to γ-maltodextrin, $(C_6)\cdot\gamma\cdot(C_6)\cdot\alpha\cdot(C_6)\cdot(C_6)$, and maltose, $(C_6)\cdot\gamma\cdot(C_6)$, the former of these, on further treatment, yielding maltose and dextrinose (Lintner's *iso*maltose), $(C_6)\cdot(C_6)$. Protodextrin I consists of four aggregates, each containing three dextrose residues, (C_6), joined by β-linkings in the following manner:



If (C_{12}) be taken to represent maltose, $(C_6)\cdot\gamma\cdot(C_6)$, then the amylogen complex is $\begin{array}{l}(C_{12})\cdot(C_6) \\ \qquad\quad | \\ (C_{12})\cdot(C_6)\end{array}\!\!>\!(C_6)\cdot(C_{12})$, and this may be written in the more condensed form $C_{18}\!<\!\begin{array}{l}C_{18} \\ \,| \\ C_{18}\end{array}$.

The starch molecule, $C_{216}H_{360}O_{180}$, consists of four conjugated amylogen residues, each of these being connected with the other three by three pairs of anhydrocarbinol linkings, three of these being between protodextrin I complexes and three between maltose

residues. The structure of the starch molecule may accordingly be conventionally represented by the plane formula:



The six linkings between the maltose residues (*m*-carbinol linkings) are resolved when amylodextrin, $C_{216}H_{372}O_{186}$, is formed from starch by the addition of 6 mols. of water. G. T. M.

Behaviour of Glycogen to Boiling Caustic Alkali. EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, **92**, 81—101).—Further experiments are given which show that, if glycogen is boiled for many (40) hours with strong potassium hydroxide (36 per cent.), it is not destroyed at all. Prolonged boiling with dilute (2 per cent.) alkali leads to a loss of about 4 per cent. W. D. H.

New Compound of the Hexamethylenetetramine Group. MARCEL DESCUDÉ (*Compt. rend.*, 1902, **135**, 693—696).—Gaseous ammonia reacts with methylene dibenzoate, as with other esters, yielding, in the first place, benzamide and methylene glycol, that is, formaldehyde and water. The formaldehyde and the ammonia produce hexamethylenetetramine; at the same time, some ammonium benzoate is formed. In the case of the dibenzoate, the reaction must be carried out in the presence of a large quantity of alcohol, but with the diacetate a smaller quantity of alcohol may be used and the yield of the tetramine is much larger; this reaction, in fact, affords a rapid method of preparing the base in a pure state.

If the alcoholic solution of the benzamide and hexamethylenetetramine be evaporated on the water-bath, these substances react forming a compound, *tribenzoyltriaminotrimethylamine*, $N(CH_2{\cdot}NH{\cdot}COPh)_3$; it has also been obtained from benzamide, formaldehyde, and ammonia; it crystallises in lustrous plates melting at 187° and has a sp. gr. 1·24; on heating, it decomposes, yielding a sublimate of benzamide. Dilute acids convert this substance into methylenedibenzamide, formaldehyde, and ammonia.

Attention is drawn to the fact that the formation of this compound under the conditions just mentioned is evidence for the constitutional formula for hexamethylenetetramine, $N(CH_2{\cdot}N{:}CH_2)_3$. K. J. P. O.

Occurrence and Properties of Choline. HEINRICH STRUVE (*Zeit. anal. Chem.*, 1902, **41**, 544—550).—See this vol., ii, 116.

Oxime of Diacetone Alcohol and a Hydroxyhexylamine. MORIZ KOHN and G. LINDAUER (*Monatsh.*, 1902, **23**, 754—764).—Diacetone alcohol oxime, which crystallises in needles and melts at 57·5—58·5°, when reduced with sodium and alcohol is converted into hydroxy-*β*-*iso*hexylamine, which boils at 174° and yields an oxalate melting at 211°; this amine is identical with that described by Kerp (Abstr., 1896, i, 448), prepared from the oxime of mesityl oxide. The amine and phenylthiocarbimide interact, forming a *thiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot OH$, which melts at 131°; on heating this with hydrochloric acid under pressure, a penthiazoline derivative, $N\ll\begin{matrix}C(NHPh)\cdot S\\ CHMe\cdot CH_2\end{matrix}\gg CMe_2$, is obtained. E. F. A.

New Base derived from Galactose. E. ROUX (*Compt. rend.*, 1902, **135**, 691—693. Compare Abstr., 1901, i, 372).—By a method very similar to that previously described (*loc. cit.*) for the preparation of dextroseamine, *galactamine*, $OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH_2\cdot NH_2$, has been obtained from galactoseoxime; the base forms a colourless, crystalline mass which is very soluble in water but not in boiling alcohol; it melts at 139° and has $[\alpha]_D$ $-2·77°$ in 10 per cent. aqueous solution, and does not exhibit mutarotation. It is a strong base, displacing ammonia. With metallic salts, it behaves as does glucamine, but does not give a crystalline compound with copper sulphate. The *oxalate*, $(C_6H_{13}O_5\cdot NH_2)_2,C_2O_4H_2,2H_2O$, crystallises in slender, arborescent needles melting at 129—130°; it loses water at 100° and, in 8 per cent. aqueous solution, has $[\alpha]_D$ $-11·28°$; the anhydrous salt, obtained from the alcoholic solution, forms acicular crystals melting at 200°. The *hydrochloride*, $C_6H_{13}O_5\cdot NH_2,HCl,H_2O$, crystallises in prismatic needles which effloresce in dry air; the anhydrous salt is an amorphous powder. The *picrate* crystallises in minute, chrome-yellow needles, the *platinichloride* in orange plates. The normal *sulphate* forms prismatic needles. *Benzylidenegalactamine*, $C_6H_{13}O_5\cdot N\colon CHPh$, prepared from benzaldehyde and galactamine, forms scales which melt and decompose at 195—196° and are easily hydrolysed by water. The *carbamide*, $C_6H_{13}O_5\cdot NH\cdot CO\cdot NH_2$, prepared from galactamine sulphate and potassium cyanate, forms rectangular plates melting at 180°; it has $[\alpha]_D$ $-12·5°$ and does not exhibit mutarotation; by sodium hypobromite, it is decomposed in the same manner as glucaminecarbamide. The *phenylcarbamide*, $C_6H_{13}O_5\cdot NH\cdot CO\cdot NHPh$, prepared from phenylcarbimide and galactamine, crystallises in long, prismatic needles melting at 219°.

Phenylcarbamidogalactamine pentaphenylcarbamate,

$$NHPh\cdot CO\cdot NH\cdot C_6H_{13}O_5(CO\cdot NHPh)_5,$$

is formed when excess of phenylcarbimide is used, and crystallises in small needles melting and decomposing at 325°. *Mercaptogalactoxazoline*, $N\ll\begin{matrix}CH_2\text{—}CH\cdot[CH\cdot OH]_3\cdot CH_2\cdot OH\\ C(SH)\cdot O\end{matrix}$, is obtained when galact-

amine is heated with carbon disulphide; it forms plates melting at 185—186°, and, like the corresponding derivative of dextrose, gives a crystalline compound with silver nitrate. K. J. P. O.

d-**Glucosamine and Chitose.** CARL NEUBERG (*Ber.*, 1902, **35**, 4009—4023).—[With HANS WOLFF.]—Chitamic acid is preferably prepared from glucosamine hydrochloride and not the hydrobromide (compare Fischer and Tiemann, Abstr., 1894, i, 167); it is sweet and has a pleasant taste, and on heating gives off vapours which colour a pine-splinter red. Chitamic acid and phenylcarbimide yield *tetrahydroxybutyl*-N-*phenylhydantoin*, which crystallises in colourless needles, becoming brown at 170° and melting at 199—201°; in aqueous solution, the compound has $[\alpha]_D + 93{\cdot}2°$. Phenylthiocarbimide and chitamic acid yield *tetrahydroxybutyl*-N-*phenylthiohydantoic acid*, which forms crystals melting at 178—180°. *Brucine glucosamate* forms insoluble crystals which become brown at 210° and melt at 228—230°. On heating chitamic acid with acetic anhydride and sodium acetate, a *compound*, $C_6H_9O_3NAc_2$, is obtained; it forms lustrous prisms melting at 125°. When *d*-glucosamic acid is reduced with phosphorus and iodine, a *compound*, $C_6H_{13}O_3N$, is formed which melts at 190—200°; on more vigorous reduction with hydriodic acid and phosphorus under pressure, 1-aminohexoic acid is obtained in a partially racemised condition (Fischer and Hagenbach, Abstr., 1902, i, 85). The *copper* salt forms pale blue leaflets.

Chitaric acid, obtained by Fischer and Tiemann's process from chitamic acid, was oxidised with hydrogen peroxide and ferrous sulphate by Fenton's method; the product was evaporated to dryness and the pentose extracted with alcohol; from the latter, the phenyl-*d*-arabinosazone was obtained. Hence chitaric acid is a derivative of *d*-arabinose or *d*-ribose. On attempting to degrade chitaric acid by Wohl's method by treatment of glucosamine hydrochloride with sodium acetate and acetic anhydride, *penta-acetylglucosamic nitrile*, $OAc{\cdot}CH_2{\cdot}[CH{\cdot}OAc]_3{\cdot}CH{\cdot}NHAc{\cdot}CN$, is formed; it crystallises in lustrous prisms melting at 118—119° (corr.), and when boiled with dilute sodium hydroxide evolves hydrocyanic acid. 2-*Aminoglucoheptonic acid* is prepared by treating chitosamine hydrochloride with potassium cyanide or ammonium cyanide; the acid was purified by conversion into the lead and finally into the copper salt, $C_7H_{13}O_7NCu$, which is a green powder; the *brucine* salt crystallises in prismatic needles, which become yellow at 160° and melt at 163—164°. The *tetrabenzoyl* derivative of 2-aminoglucoheptonic acid forms aggregates which begin to decompose at 85° and melt at 101—110°. By the oxidation of this acid with fuming nitric acid, pentahydroxypimelic acid was formed and isolated as the calcium salt.

[With WILHELM NEIMANN.]—On treatment of chitosoxime with silver nitrite, a substance is obtained which yields a lead *compound*, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH{:}N{\cdot}OH,3PbO$. *Methylchitoside*, prepared from chitose syrup, crystallises with H_2O in rhombohedra. *Tribenzoylchitose* is obtained by the Schotten-Baumann method, and crystallises in colourless needles melting at 116°. Chitoheptonic acid is prepared

from chitose syrup and hydrocyanic acid, and subsequent hydrolysis of the product with lead carbonate; the *barium* salt is an amorphous, yellow powder. The *dibenzoyl* derivative crystallises in small octahedra which begin to decompose at 110° and melt at 117—120°.

K. J. P. O.

Physiological Relations of Derivatives of Proteids containing Sulphur. I. Constitution of Cystin. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1902, 3, 1—46. Compare Abstr., 1902, i, 731, and Neuberg, Abstr., 1902, i, 743).—Baumann ascribed to cystein, obtained from the cystin-stone of cystinuria, the formula $SH\cdot CMe(NH_2)\cdot CO_2H$ (cystin bears to cystein the relation of a disulphide to a mercaptan); the cystein, prepared by Mörner's method (Abstr., 1900, i, 128) from hair, is shown to have the constitution $SH\cdot CH_2\cdot CH(NH)_2\cdot CO_2H$ (α-amino-β-thiolpropionic acid), for it can be converted on the one hand into taurine,

$$SO_3H\cdot CH_2\cdot CH_2\cdot NH_2,$$

and on the other hand into the disulphide of β-thiolpropionic acid, $SH\cdot CH_2\cdot CH_2\cdot CO_2H$ (compare Neuberg, *loc. cit.*).

Cystin is converted by treatment with alcohol and hydrochloric acid into the *hydrochloride* of the ethyl ester of cystin,

$$S_2[CH_2\cdot CH(NH_2)\cdot CO_2Et]_2,3HCl,$$

which crystallises in colourless needles decomposing at 185°.

Cystinhydantoic acid, previously obtained by Brenzinger (Abstr., 1892, 1111) as anhydride, by acting on cystin with potassium cyanate, has been isolated as *barium* salt, $C_8H_{12}O_6N_4S_2Ba,H_2O$, which is an amorphous, hygroscopic powder. The *silver* salt, $C_8H_{12}O_6N_4S_2Ag_2,Ag_2O$, is a yellow powder very sensitive to light. On reducing the dichloro-derivative of cystin, first obtained by Jochem (Abstr., 1901, i, 129), by the action of sodium nitrite on a solution of cystin in concentrated hydrochloric acid, β-thiolpropionic acid is formed, which was not isolated but converted directly into the *disulphide*, $(C_3H_5O_2)_2S_2$, by oxidation with ferric chloride; the latter melts at 154° and is identical with the compound obtained from β-iodopropionic acid.

Cysteic acid (α-amino-β-sulphopropionic acid),

$$SO_3H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

prepared by the action of bromine on cystin or cystein, is purified by conversion into the copper salt and crystallises either in anhydrous octahedra or in prismatic needles with H_2O; it behaves as a monobasic acid, decomposes at 260°, and has $[\alpha]_D$ +8·66 when anhydrous, and +7·46 when hydrated. The *potassium* salt, $C_3H_6O_5NSK,H_2O$, is a crystalline powder; the *barium* salt is amorphous; the *copper* salt,

$$C_3H_6O_5NS\cdot Cu\cdot OH,$$

forms deep blue crystals; the *zinc* salt crystallises with $3H_2O$. By heating cysteic acid under pressure with water at 235° for 2 hours, it is very largely converted into taurine. When heated with barium hydroxide at 150°, a small quantity of serine (α-amino-β-hydroxypropionic acid) is formed.

The author discusses the origin and the fate of cystin in the organism.

K. J. P. O.

βγ-Diaminoadipic Acid. WILHELM TRAUBE (*Ber.*, 1902, **35**, 4121—4128).—The double lactam,

$$\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{N{=\!=\!=}C\cdot CH(CO_2Et)}\\ \mathrm{CH(CO_2Et)\cdot C{=\!=\!=}N}\end{array}\Big\rangle\mathrm{CO},$$

produced by the action of cyanogen on ethyl sodiomalonate (Abstr., 1898, i, 241), is reduced by sodium amalgam to *βγ-diamino-αδ-dicarboxyadipic acid*, $\mathrm{CH(CO_2H)_2\cdot CH(NH_2)\cdot CH(NH_2)\cdot CH(CO_2H)_2}$, which crystallises in rhombic tablets; the *silver* salt is precipitated in the form of colourless needles. The *double lactam*,

$$\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{-}CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH{-}NH}\end{array}\Big\rangle\mathrm{CO},$$

of *βγ-diaminoadipic acid*, prepared by heating the preceding compound at 180°, crystallises with H_2O from dilute alcohol in long, colourless needles, forms a *platinichloride* which crystallises in long, yellow needles, and an unstable, yellow, crystalline *nitroso*-derivative. *βγ-Diaminoadipic acid*, prepared by hydrolysing the lactam with barium hydroxide and precipitating the barium with carbon dioxide, separates with $2H_2O$ in well-formed crystals, is only slightly soluble in cold water, but dissolves readily in mineral acids, forms a readily soluble *hydrochloride* and a soluble *platinichloride* which separates in stout, yellow prisms.

The *monolactam*, $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{-\!-\!-}CH\cdot CBr(CO_2H)_2}\\ \mathrm{CBr(CO_2H)\cdot CH\cdot NH_2}\end{array}$, of αδ-dibromo-βγ-diaminodicarboxyadipic acid, prepared by the action of bromine on diaminodicarboxyadipic acid, crystallises from alcohol in minute needles. When heated with dilute hydrogen chloride, it loses carbon dioxide and yields the *dilactam*, $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{-\!-}CH\cdot CHBr}\\ \mathrm{CHBr\cdot CH{-\!-}NH}\end{array}\Big\rangle\mathrm{CO}$, of *αδ-dibromo-βγ-diaminoadipic acid*, which is insoluble in ammonia, but dissolves in alkalis and is reprecipitated by-acids in minute, colourless needles. Ethyl βγ-di-imino-αδ-dimethyldicarbethoxyadipate is reduced by sodium amalgam to the *amino-imino-ester-acid*,

$$\mathrm{CO_2H\cdot CMe(CO_2Et)\cdot CH(NH_2)\cdot C(\colon NH)\cdot CMe(CO_2H)_2},$$

which crystallises in minute, colourless needles and melts with liberation of gas at 139—140°. The fused product is a *monolactam*, $C_{11}H_{16}O_5N_2$, formed by liberation of CO_2 and H_2O, and crystallises from hot water in colourless prisms melting without decomposition at 199°.

T. M. L.

Cadmium, Zinc, and Bismuth Cobalticyanides. TH. FISCHER and A. CUNTZE (*Chem. Zeit.*, 1902, **26**, 872—873).—*Cadmium cobalticyanide*, $2Cd_3Co_2(CN)_{12},15H_2O$, is prepared by boiling a dilute solution of cadmium chloride with a quantity of potassium cobalticyanide insufficient to precipitate the cadmium; it is a white, amorphous powder which loses $10H_2O$ when dried in an exhausted desiccator over sulphuric acid; the salt is soluble in ammonia and ammonium chloride and is decomposed only on boiling with mineral acids. The corresponding *zinc* salt, $Zn_3Co_2(CN)_{12},12H_2O$, is a white, amorphous powder. The *bismuth* salt, $BiCo(CN)_6,5H_2O$, is crystalline, and when dried over sulphuric acid is converted into a salt $2BiCo(CN)_6,7H_2O$.

The cobalticyanides of cadmium and zinc are converted into alkali double salts when they are heated with a concentrated solution of alkali cobalticyanide under pressure at 160°. The following salts were prepared in this manner: $KCdCo(CN)_6$, crystals, $NaCdCo(CN)_6,H_2O$, quadratic leaflets, $KZnCo(CN)_6,3H_2O$, quadratic leaflets,

$NaZnCo(CN)_6,H_2O$,

quadratic plates. The following additive ammonia compounds were obtained by dissolving the cadmium and zinc salts in ammonia and precipitating with alcohol: $Cd_3Co_2(CN)_{12},4NH_3,2H_2O$; $Cd_3Co_2(CN)_{12},9NH_3,2H_2O$; $Cd_3Co_2(CN)_{12},7NH_3$; $Cd_3Co_2(CN)_{12},5NH_3,3H_2O$; $Zn_3Co_2(CN)_{12},10NH_3,9H_2O$; $Zn_3Co_2(CN)_{12},6NH_3$ with H_2O, $3H_2O$, or $5H_2O$; $Zn_3Co_2(CN)_{12},5NH_3$.

By treating the cadmium salts with dilute hydrochloric acid, an insoluble salt, $Cd_3Co_2(CN)_{12},NH_4Cl,4H_2O$, is always formed.

K. J. P. O.

Physico-chemical Studies on the Acid Function of the Oximino-group. I. Electrical Conductivity of Oximinocyanoacetic Esters. PAUL THIEBAUT MULLER (*Bull. Soc. chim.*, 1902, [iii], 27, 1011—1014).—The electrical conductivities (μ_∞) of the sodium derivatives of the methyl, ethyl, and propyl esters of oximinocyanoacetic acids (Abstr., 1894, i, 317) are respectively 89·41, 86·62, and 83·55, whence those of the free oximino-esters are 383·37, 380·58, and 377·51 respectively. The corresponding affinity constants ($K \times 100$) are 0·00315, 0·00228, and 0·00230. Comparing these values with that of acetic acid ($K \times 100 = 0·0018$), it is seen that the oximino-esters are slightly stronger than this acid, and in conformity with this view it has been found possible to titrate them with alkalis, using phenolphthalein as indicator, to calculate their mol. conductivities from those of the sodium derivatives on the assumption that they are monobasic acids, and to obtain normal cryoscopic measurements with aqueous solutions of their sodium derivatives. T. A. H.

Physico-chemical Studies on the Acid Function of the Oximino-group. II. Optical Properties of the Oximinocyanoacetic Esters. PAUL THIEBAUT MULLER (*Bull. Soc. chim.*, 1902, [iii], 27, 1014—1018).—Methyl oximinocyanoacetate, $CN\cdot C(NOH)\cdot CO_2Me$, has mol. refractions 28·26, 28·90, 29·87, and 28·52 for the α-, β-, and γ-hydrogen and D lines respectively, and mol. dispersion 1·61 between the α- and γ-hydrogen lines. Methyl methyloximinocyanoacetate, $CN\cdot C(NOMe)\cdot CO_2Me$, has a sp. gr. 1·1768 at 20° and mol. refractions 32·75, 33·63, 34·21, and 32·99 for the α-, β-, γ-, and D lines respectively, and mol. dispersion 1·46 between the α- and γ-lines. Methyl ethyloximinocyanoacetate has a sp. gr. 1·1240 at 20° and mol. refractions 37·57, 38·56, 39·21, and 37·86 respectively for the four lines already mentioned, and mol. dispersion ($M\gamma - M\alpha$) 1·64.

Ethyl oximinocyanoacetate, $CN\cdot C(NOH)\cdot CO_2Me$, has mol. refractions 32·83, 33·54, 34·71, and 33·02 respectively for the same four lines, and mol. dispersion 1·88 between the α- and γ-hydrogen lines. Ethyl ethyloximinocyanoacetate, $CN\cdot C(NOEt)\cdot CO_2Et$, has sp. gr. 1·0818 at 20° and mol. refractions 42·18, 43·24, 43·93, and 42·48 respectively for the

four reference lines, and mol. dispersion 1·60 between the α- and γ-lines. Ethyl methyloximinocyanoacetate has sp. gr. 1·1255 at 20°, mol. refractions 37·44, 38·41, 39·04, and 37·71 for the reference lines, and mol. dispersion 1·60.

The observed mol. refractions differ from the calculated values by quantities varying from 1·46 to 1·98, whilst the differences between the observed and calculated values for the mol. dispersions vary from 0·60 to 0·67. The differences due to homology are normal and equal to 4·5 to 4·7 (calculated value 4·6), so that there can be no question of difference in structure between the esters and their alkyl derivatives. It is suggested that the abnormality of the observed optical constants is due to the mutual influence of the –CN and $\colon$NOR groups in the molecule. T. A. H

Physico-chemical Studies on the Acid Function of the Oximino-group. III. Sodium Salts of *iso*Nitroso-derivatives and the Diagnosis of Pseudo-acids. Paul Thiebaut Muller (*Bull. Soc. chim.*, 1902, [iii], **27**, 1019—1022).—The sodium derivative of methyloximinocyanoacetate has the mol. refractions 31·59, 32·94, and 31·99 for the α- and γ-hydrogen and D lines respectively, whilst the sodium derivative of the corresponding ethyl ester has mol. refractions 36·12, 37·65, and 36·53 for the same lines. In both cases, the differences in the refractions of the sodium derivatives of the free esters are above 3, instead of the calculated values 1·5—1·7. This abnormality is due, not to ionisation of the sodium derivative, but probably to a difference in structure of the ester and its sodium compound; for the latter, one of the following formulæ is suggested:

$$\mathrm{CN{\cdot}\overset{\overset{N\cdot O}{\|\quad|}}{C}{\cdot}C(OEt){\cdot}ONa} \quad \text{and} \quad \mathrm{CN{\cdot}C}\!\!<\!\!\begin{array}{l}\mathrm{C(OEt)\text{-}}\\ \mathrm{N(ONa)}\end{array}\!\!>\!\!\mathrm{O},$$

and in support of such cyclic structures for the metallic derivatives it is pointed out that whilst the free solid ester is colourless, its solutions are faintly yellow and its sodium compound distinctly yellow. The first formula contains an asymmetric carbon atom, but the resolution of the sodium derivative has not been accomplished. It is suggested that a difference greater than 3 between the mol. refractions of an acid and its salt indicates that the latter is a pseudo-acid. T. A. H.

Diazotisation of Hydrazine. Mario Betti (*Gazzetta*, 1902, **32**, ii, 146—152).—The many attempts previously made to transform both the aminic groups of hydrazine into diazo-groups by the action of nitrous acid, and thus to obtain a derivative of the compound NH:N·N:NH, have been unsuccessful, owing to the extreme facility with which the compound NH_2·N:N·OH, furnished by the diazotisation of one of the aminic groups of hydrazine, is transformed into azoimide. By using instead of nitrous acid one of its derivatives, namely, ethyl nitrosoacetoacetate, which V. Meyer has shown can act in either of the tautomeric forms, COMe·CH(NO)·CO_2Et and COMe·C(N·OH)·CO_2Et, the author has, however, been enabled to diazotise both the aminic groups of hydrazine and to obtain a compound containing a chain of four nitrogen atoms; ·N:N·N:N·.

Ethyl bisdiazoacetate, $N_4(CHAc \cdot CO_2Et)_2$, is prepared by adding to ethyl acetoacetate diluted with water, successively and with cooling, normal sodium hydroxide solution, a concentrated solution of sodium nitrite and normal hydrochloric acid solution, and, after 12 hours, a saturated solution of hydrazine sulphate; it is insoluble in water or benzene, but from alcohol it separates in large, shining, cubic crystals and from dilute alcohol in lemon-yellow, nacreous leaves, which melt and decompose at 197°; it is soluble in moderately concentrated alkali hydroxide solutions, from which it is reprecipitated unchanged on the addition of acids; the free acid could not be obtained, the action of dilute acids on the ester yielding a crystalline compound to be further investigated; the molecular weight, determined cryoscopically in phenol, is 278. The *sodium* salt, $C_{12}H_{16}O_6N_4Na_2$, which in aqueous solution has a strongly alkaline reaction, separates as a yellowish, crystalline precipitate, decomposing without melting when heated. T. H. P.

Magnesium Organic Compounds as a Test for the Hydroxyl Group. L. Tschugaeff (*Ber.*, 1902, 35, 3912—3914).—Dry hydroxyl compounds, when mixed with ethereal magnesium methiodide, $CH_3 \cdot MgI$, liberate methane; this qualitative test, which is best performed in a nitrometer, may perhaps be made the basis of a quantitative method. The separation of alcohols from hydrocarbons can be effected by combining with magnesium methiodide, distilling off the hydrocarbons, and decomposing the residue with water. T. M. L.

Law of Substitution in Aromatic Compounds. Bernhard Flürscheim (*J. pr. Chem.*, 1902, [ii], 66, 321—331).—Vorländer's rule that benzene compounds which yield *meta*-substitution derivatives have an unsaturated atom directly attached to the benzene nucleus (Abstr., 1902, i, 328) is contradicted by the behaviour of such substances as benzylidene chloride and phenylaminoacetic acid. Adopting Werner's conception of valency, the author develops a theory of the cause of substitution in the *meta*-, *ortho*-, and *para*-positions respectively.

Bromocyanophenylnitromethane, $CN \cdot CPhBr \cdot NO_2$, formed by the action of bromine on the sodium derivative of *iso*nitrobenzyl cyanide (Abstr., 1902, i, 541), is a pungent, yellow oil, which decomposes on distillation, yielding two colourless, crystalline products melting at 35° and 100—110°, and, on nitration and subsequent oxidation with potassium permanganate, yields a mixture of *p*-nitrobenzoic acid and benzoic acid. G. Y.

Tetrachlorodinitrobenzene. C. Loring Jackson and H. A. Carlton (*Ber.*, 1902, 35, 3855—3857).—1 : 2 : 3 : 5-*Tetrachloro*-4 : 6-*dinitrobenzene*, obtained by boiling 1 : 2 : 3 : 5-tetrachloronitrobenzene with a mixture of nitric and sulphuric acids, crystallises from acetic acid in large, white rhombs and melts at 161—162°; it interacts with sodium ethoxide in alcoholic benzene solution at the ordinary temperature, giving a *chlorodinitrophloroglucinol triethyl ether*,

$$C_6Cl(NO_2)_2(OEt)_3,$$

which crystallises from alcohol in long, white needles melting at 76°, together with a *chlorodinitrophloroglucinol diethyl ether*,

$$OH\cdot C_6Cl(NO_2)_2(OEt)_2;$$

this crystallises in thin, yellow needles, melts at 102—103°, and gives an anhydrous *barium* salt. The foregoing substances only form 10 per cent. of the product of the action of the ethoxide, the principal substance obtained being an oil which is volatile with steam, but decomposes when distilled alone under the ordinary pressure. W. A. D.

Electrolytic Reduction of *o*- and *p*-Nitrobenzenesulphonic Acids in Alkaline Solution. KARL ELBS and TH. WOHLFAHRT (*Zeit. Elektrochem.*, 1902, 8, 789—791).—A solution of potassium *p*-nitrobenzenesulphonate, when reduced in the manner previously described (Abstr., 1899, i, 270), yields the potassium salt of azobenzene-*p*-disulphonic acid. The yield is nearly quantitative. Further reduction gives the hydrazo-compound.

Potassium-*o*-nitrobenzenesulphonate gives an amorphous, green colouring matter and small quantities of *o*-aminobenzenesulphonic acid and benzidine-*o*-disulphonic acid.

The ammonium salt gives more than 80 per cent. of the theoretical quantity of *o*-aminobenzenesulphonic acid and a little benzidine-*o*-disulphonic acid. T. E.

Polymerisation. I. Polymerisation of Styrene and of Cyanic Acid. ABRAHAM KRONSTEIN (*Ber.*, 1902, 35, 4150—4153).—Polymerisations which occur without the formation of any intermediate product are termed by the author *euthymorphous*, those in which an intermediate compound is produced, *mesomorphous*. The polymerisation of styrene to metastyrene belongs to the mesomorphous group, since, although the polymerised product metastyrene is insoluble in styrene, yet the styrene gradually increases in viscosity before solidifying, a product being formed which is soluble in styrene (see the following abstract). The conversion of cyanic acid into cyamelide belongs to the euthymorphous group, as does that of *cyclo*pentadiene, di*cyclo*pentadiene, and ethyl cinnamate. When *cyclo*pentadiene is heated at 160° in a sealed tube, it gradually changes into a yellowish mass of an insoluble polymeride, which is reconverted into the original *cyclo*pentadiene by heat. Di*cyclo*pentadiene undergoes a similar change, but it has not yet been decided whether the resulting polymeride is identical with that obtained from *cyclo*pentadiene. The gradual change of ethyl cinnamate into an amorphous, insoluble, colourless polymeride, which sometimes occurs, also appears to take place without the formation of any intermediate product. A. H.

Polymerisation. II. Mesomorphous Polymerisation (Type, Styrene). ABRAHAM KRONSTEIN (*Ber.*, 1902, 35, 4153—4157. Compare the foregoing abstract).—The polymerisation of styrene occurs in two stages: (1) a product is formed which is soluble in styrene, and (2) this reacts with an equal weight of unaltered styrene, forming the insoluble metastyrene. The new intermediate product may be isolated by pouring the viscous mass, before solidification has commenced, into

benzene and adding alcohol, which precipitates an oil, and this gradually solidifies. This substance is also formed when styrene is polymerised in solution in hydrocarbons, and was mistaken by Berthelot for metastyrene. A. H.

Sulphonic Acids of 2 : 4-Dinitrostilbene. RICHARD ESCALES (*Ber.*, 1902, 35, 4146—4149).—When 2 : 4-dinitrostilbene is heated on the water-bath with sulphuric acid, it yields *dinitrostilbenesulphonic acid*, a brown, crystalline mass, which commences to melt at 70° and decomposes at 112°. It is sparingly soluble in water, readily so in ethyl acetate. The *barium* salt is almost insoluble, even in hot water. When reduced, the sulphonic acid yields a nitroamino-derivative and finally 2: 4-diaminostilbenesulphonic acid.

Fuming sulphuric acid converts dinitrostilbene into 2 : 4-*dinitrostilbenedisulphonic acid*, which forms a light yellow, crystalline powder melting at about 125°, although some preparations were found to melt at 83—85°. The acid is readily soluble in water and forms a readily soluble *barium* salt, $C_{14}H_8O_{10}N_2S_2Ba$, crystallising with $4H_2O$. The *benzidine* salt, $C_{26}H_{22}O_{10}N_4S_2$, crystallises in slender, light yellow needles which do not melt below 280°. Solutions of the acid yield no precipitates with barium, copper, mercurous, or silver salts. The acid is stable towards alkaline permanganate in the cold, and by reduction is converted into a nitroamino-derivative and a diaminodisulphonic acid. A. H.

Formation of Trioxymethylene by Direct Oxidation of Aromatic Compounds containing a β-Allyl Side Chain. MARC TIFFENEAU (*Bull. Soc. chim.*, 1902, [iii], 27, 1066—1068).—When aromatic substances of the type $CRR'{:}CH_2$, where R is an aromatic, and R′ either an aliphatic or aromatic group, are oxidised by air, formaldehyde is produced and deposited as its polymeride trioxymethylene. The latter has been obtained in this way from β-allylbenzene, β-allyl-*m*- and *p*-toluenes, *as*-diphenylethylene, and *as*-phenyl-*p*-tolylethylene.

Limonene, which is generally represented as containing a β-allyl-side chain, furnishes no trioxymethylene on oxidation by air ; other reactions of this substance are also not in harmony with such a structure (compare Semmler, Abstr., 1901, i, 732). T. A. H.

Triphenylmethyl. Condensation to Hexaphenylethane. MOSES GOMBERG (*Ber.*, 1902, 35, 3914—3920).—The hexaphenylethane recently described by Ullmann and Borsum (Abstr., 1902, i, 755) is formed in small quantity in the preparation of triphenylchloromethane from carbon tetrachloride and benzene, and is also obtained in small amount when a solution of triphenylmethyl in glacial acetic acid is treated with sodium nitrite. When an acetic acid solution of triphenylchloromethane is treated in the cold with either molecular silver, granulated tin, or zinc dust or strips, hexaphenylethane is not produced, but if the solution is heated with these metals, it is formed in large amount, no triphenylmethyl being found in the product. The formation of hexaphenylethane in these cases is

probably a secondary reaction due to the polymerisation of the triphenylmethyl which is first formed, and this polymerisation can be brought about quantitatively by dissolving the product of the action of zinc on triphenylchloromethane in warm chloromethyl ethyl ether.

A. H.

Some Products of the Oxidation of Aniline by Atmospheric Oxygen. CONSTANTIN I. ISTRATI (*Compt. rend.*, 1902, **135**, 742—744).—When a current of dry air is aspirated through boiling aniline for 10 hours, the liquid becomes brown; after 10 days, it is black and syrupy, and on cooling deposits black crystals. In about 25 days, the mass is completely solid. The solid is partially soluble in cold alcohol. The alcoholic solution contains an unstable, colourless solid which melts at 110—112° and oxidises readily to a red, insoluble substance melting at 207—208°.

Part of the substance insoluble in alcohol is soluble in cold chloroform. The substance extracted by the chloroform is red, melts at 207—208°, and appears to have the composition $O[C_6H_2(NHPh)_3]_2$; when treated with nitrous acid, it gives a red nitroso-compound melting at 190—197°.

From the residue insoluble in cold alcohol and chloroform, long, colourless needles melting at 238—239° and containing C = 74·43, H = 5·96, N = 13·23 per cent. have been isolated, and, by extraction with hot alcohol, a colourless compound melting at 251°, which appears to have the composition $C_6\left(<\begin{matrix}NPhO\\ |\\ NPhO\end{matrix}\right)_3$, and gives a nitro-derivative melting at 247°.

J. McC.

Reactions of Formaldehyde. CARL GOLDSCHMIDT (*Chem. Zeit.*, 1902, **26**, 967. Compare Abstr., 1900, i, 436).—By the action of excess of formaldehyde and hydrobromic acid on monomethylaniline, a compound, $NPhMe{\cdot}CH_2Br$, is obtained; it melts at 250° and with sodium hydroxide gives the *p*-anhydroamino-alcohol. On using hydriodic acid, an insoluble base, $CH_2<\begin{matrix}C_6H_4{\cdot}NMe{\cdot}CH_2\\ C_6H_4{\cdot}NMe{\cdot}CH_2\end{matrix}>O$, is formed.

K. J. P. O.

Condensation of Nitro-derivatives of Benzyl Chloride with Naphthylamines. GEORGES DARIER and E. MANNASSEWITCH (*Bull. Soc. chim.*, 1902, 27, [iii], 1055—1066).—o-*Nitrobenzyl-a-naphthylamine*, $C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, is formed together with a small quantity of *di-o-nitrodibenzyl-a-naphthylamine* (which crystallises in orange prisms melting at 148°) by the interaction of *o*-nitrobenzyl chloride with *a*-naphthylamine in alcohol. It crystallises in golden-yellow, prismatic needles, melts at 97°, and is soluble in ether, chloroform, benzene, or acetic acid. The sulphate and hydrochloride are dissociated by water. The *acetyl* derivative crystallises in lustrous, colourless spangles and melts at 130°. Reduction of o-*nitrobenzyl-a-naphthylamine* or of its acetyl derivative gives a minute quantity of a crystalline base melting at 129°.

o-*Nitrobenzyl-β-naphthylamine*, similarly obtained, forms orange spangles, melts at 162°, and is soluble in benzene, chloroform, or

carbon disulphide. Its salts are immediately decomposed by water. The *acetyl* derivative crystallises in large, colourless prisms and melts at 117—118°. On reduction, the parent substance gives a diacid base, $C_{17}H_{16}N_2$, which crystallises in silver-grey spangles, melts at 110—111°, and is soluble in alcohol, ether, or benzene. With acetic anhydride this furnishes a mixture of a *diacetyl* with a *triacetyl* derivative. When diazotised, a diazo-compound is produced, which couples readily with phenols, aminophenols, and naphthols, giving a series of reddish dyes.

m-*Nitrobenzyl-α-naphthylamine* forms small, yellow prisms, melts at 94°, and is soluble in ether, light petroleum, or cold alcohol. The *acetyl* derivative forms yellow needles which melt at 109—110°.

m-*Nitrobenzyl-β-naphthylamine* forms yellow needles melting at 80°, and, with acetic anhydride, furnishes an *acetyl* derivative crystallising in small, yellow prisms melting at 104—105°.

p-*Nitrobenzyl-α-naphthylamine* crystallises in light orange-coloured spangles, melts at 126—127°, and is soluble in ether or benzene. The salts are hydrolysed by water. The *acetyl* derivative separates from alcohol in white, silky needles, melts at 112—113°, and is readily soluble in benzene or chloroform. On reduction, *p*-nitrobenzyl-α-naphthylamine gives rise to p-*aminobenzyl-α-naphthylamine*, which is a colourless oil with a slight aromatic odour; it darkens rapidly in air. The *triacetyl* derivative forms colourless prisms and melts at 216°. The diazotised base couples with phenols, naphthols, &c., furnishing brick-red to violet-red dyes.

p-*Nitrobenzyl-β-naphthylamine* separates from its concentrated alcoholic solution in red, pyramidal crystals, and from more dilute solutions in brilliant, yellow spangles. The latter, when heated at 100—110°, becomes converted into the red variety and then melts at 121·5°. It is soluble in benzene or ether. The salts are dissociated by water; the *acetyl* derivative is amorphous. On reduction p-*aminobenzyl-β-naphthylamine* is formed; this is a liquid which is readily oxidised when exposed to the atmosphere, and dissolves easily in ether or benzene; the ethereal solution possesses a faint fluorescence. The *hydrochloride* forms whitish-yellow needles. The *triacetyl* derivative crystallises in microscropic needles and melts at 250—251°. When diazotised and coupled with naphthols and their sulphonic acids, there is formed a series of cherry-red to orange-brown dyes. The dyes obtained from these isomeric amines are not sensitive to acids and alkalis, they resemble those similarly prepared from the naphthylamines in dyeing wool directly, but the shades obtained are not bright.

T. A. H.

Imino-ψ-quinols. Eugen Bamberger (*Ber.*, 1902, **35**, 3886—3892).—When *m*-xylylhydroxylamine is left with 5 per cent. sulphuric acid for 10 hours at 0° and then extracted with ether, a considerable quantity of *m*-xylo-ψ-quinol, $OH\cdot CMe<\substack{CH:CMe \\ CH=CH}>CO$, is obtained; after neutralising with concentrated sodium hydroxide solution at −5° and again extracting fractionally with ether, more *m*-xylo-ψ-quinol and a considerable quantity of *imino*-m-*xylo-ψ-quinol*,

$$\mathrm{OH{\cdot}CMe}\Big<\begin{matrix}\mathrm{CH{:}CMe}\\ \mathrm{CH{=}CH}\end{matrix}\Big>\mathrm{C{:}NH},$$

are isolated in different fractions. The latter substance was purified by repeatedly precipitating its *hydrochloride* from absolute alcohol by means of ether; the salt was not, however, obtained quite pure. The hydrochloride dissolves in water or alcohol with an acid reaction, and on adding alkali and extracting with ether the base is obtained as a shellac-like, semi-solid mass; on boiling with water, the imino-ψ-quinol loses ammonia and gives *m*-xylo-ψ-quinol, which crystallises from light petroleum in colourless, vitreous prisms and melts at 73—73·5°.

Imino-*m*-xylo-ψ-quinol is converted by bleaching powder into a *chloroimide* and by sodium nitrite into a *nitrosoamine* which gives Liebermann's reaction; with *p*-nitrophenylhydrazine, *p*-nitrobenzene-azo-*m*-xylene, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3Me_2$, is obtained.

Similar attempts to prepare iminotolu-ψ-quinol failed to give definite results.

From the foregoing results, the transformation of *m*-xylylhydroxylamine into *p*-xyloquinol by dilute sulphuric acid (Abstr., 1901, i, 529—531) probably takes place in the following stages:

$$\mathrm{C_6H_3Me_2{\cdot}NH{\cdot}OH} \longrightarrow \left[\mathrm{C_6H_3Me_2{\cdot}N=}\right] \longrightarrow$$

$$\mathrm{OH{\cdot}CMe}\Big<\begin{matrix}\mathrm{CH{:}CMe}\\ \mathrm{CH{=}CH}\end{matrix}\Big>\mathrm{C{:}NH}$$

Imino-*m*-xylo-ψ-quinol.

$$\mathrm{OH{\cdot}CMe}\Big<\begin{matrix}\mathrm{CH{:}CMe}\\ \mathrm{CH{=}CH}\end{matrix}\Big>\mathrm{CO} \longrightarrow \mathrm{OH{\cdot}C}\Big<\begin{matrix}\mathrm{CH{\cdot}CMe}\\ \mathrm{CMe{:}CH}\end{matrix}\Big>\mathrm{C{\cdot}OH}$$

m-Xylo-ψ-quinol. *p*-Xyloquinol.

W. A. D.

Behaviour of Anthranil, Phenylhydroxylamine and *o*-Hydroxylaminobenzaldoxime towards Hydroxylamine and Air. EUGEN BAMBERGER (*Ber.*, 1902, 35, 3893—3898).—Oxygen has no action on anthranil suspended in water, neither does it convert hydroxylamine into nitrous acid; the latter statement was proved by the fact that diazoaminobenzene is not formed on shaking an aqueous solution of hydroxylamine hydrochloride and sodium hydroxide with aniline in a vessel filled with oxygen. Anthranil with hydroxylamine alone gives *o*-hydroxylaminobenzaldoxime (compare Bamberger and Demuth, Abstr., 1902, i, 95, 127).

Phenylhydroxylamine, in presence of hydroxylamine and air, is partly reduced to aniline and partly oxidised to azoxybenzene, whilst benzene-azohydroxyanilide, $OH{\cdot}NPh{\cdot}N_2Ph$ (Bamberger and Rising, Abstr., 1901, i, 529), and phenylazoimide, PhN_3, are also formed. The production of these compounds is due to the following reactions.

Phenylhydroxylamine is oxidised to nitrosobenzene which, with hydroxylamine, gives *iso*diazobenzene hydroxide; this then combines

either with phenylhydroxylamine to form benzeneazohydroxyanilide, $N_2Ph\cdot OH + NHPh\cdot OH = OH\cdot NPh\cdot N_2Ph + H_2O$, or with hydroxylamine to form phenylazoimide, $N_2Ph\cdot OH + NH_2\cdot OH = PhN_3 + H_2O$.

The foregoing facts indicate that the transformation of anthranil by hydroxylamine and air takes place thus: *o* hydroxylaminobenzaldoxime is first formed by the action of hydroxylamine, and is oxidised to *o*-nitrosobenzaldoxime, which combines with hydroxylamine giving *o*-*iso*diazohydroxybenzaldoxime,

$$NO\cdot C_6H_4\cdot CH{:}N\cdot OH + NH_2\cdot OH = OH\cdot N_2\cdot C_6H_4\cdot CH{:}N\cdot OH.$$

The latter is then converted into *o*-azimidobenzaldoxime,

$$OH\cdot N_2\cdot C_6H_4\cdot CH{:}N\cdot OH + NH_2\cdot OH = N_3\cdot C_6H_4\cdot CH{:}N\cdot OH + 2H_2O.$$

The correctness of these views is shown by the production of *o*-azimidobenzaldoxime along with *o*-azoxybenzaldoxime and *o*-aminobenzaldoxime by the action of hydroxylamine and air on *o*-hydroxylaminobenzaldoxime.

W. A. D.

Electrolytic Reduction of *m*-Nitrophenol in Alkaline and in Acid Solutions. ERICH KLAPPERT (*Zeit. Elektrochem.*, 1902, 8, 791—792).—When *m*-nitrophenol is reduced electrolytically in alkaline solution, *m*-azophenol is formed (m. p. 204°); but when sulphuric acid is employed as solvent, *m*-aminophenolsulphonic acid is produced.

T. E.

Phenyl and Benzyl Succinates. CARL A. BISCHOFF and AUGUST VON HEDENSTRÖM (*Ber.*, 1902, 35, 4073—4079).—Phenyl succinate melts at 121°, boils at 222·5° under 15 mm. pressure, and on nitration gives a mixture of *o*- and *p*-nitrophenyl succinates, the para-compound predominating. Attempts to condense phenyl succinate with *s*-diphenylethylenediamine and with catechol gave only phenol and resinous products, but *catechol succinate*, $C_6H_4<\begin{matrix}O\cdot CO\cdot CH_2\\ O\cdot CO\cdot CH_2\end{matrix}$ or

$$C_6H_4<\begin{matrix}O\\O\end{matrix}>C<\begin{matrix}CH_2\\CO-\end{matrix}>CH_2,$$

was obtained on heating succinyl chloride with catechol at 80—100°; it crystallises from ethyl oxalate or ethylene bromide and melts at 184—190°. With resorcinol, phenyl succinate gave no definite product, but with quinol, *quinol succinate*, $C_{10}H_8O_4$, is obtained; it is insoluble in all solvents, melts at 267—269°, and is also formed on heating succinyl chloride with quinol at 110°.

Phenyl hydrogen succinate, $CO_2H\cdot C_2H_4\cdot CO_2Ph$, obtained by carefully mixing succinic anhydride with phenol, crystallises from a mixture of benzene and light petroleum in stellate aggregates of needles, melts at 98°, and dissociates into its constituents at higher temperatures.

Phenyl benzyl succinate, $CO_2Ph\cdot C_2H_4\cdot CO_2\cdot CH_2Ph$, prepared by heating silver monophenyl succinate with benzyl chloride in boiling toluene, crystallises from light petroleum in stellate masses of needles and melts at 51°.

Benzyl hydrogen succinate, obtained along with the dibenzyl ester by boiling succinic anhydride with benzyl alcohol, crystallises from a mixture of light petroleum and benzene in lustrous scales and melts at

59°. The dibenzyl ester is best prepared by heating succinic acid and benzyl alcohol for 1 hour at 180—190°; it melts at 41—44° and boils at 238° under 14 mm. pressure. W. A. D.

Aryl Esters of Succinic Acid. Carl A. Bischoff and August von Hedenström (*Ber.*, 1902, 35, 4079—4084).—The following esters were prepared by heating the phenol with succinic acid and phosphorus oxychloride.

o-*Tolyl succinate*, $C_2H_4(CO_2\cdot C_6H_4Me)_2$, from *o*-cresol, is a thick oil which boils at 238—240° under 5 mm. pressure; the m-*tolyl ester* crystallises from dilute alcohol in needles and melts at 60°, and the *p*-ester in leaflets melting at 121°.

The *xylyl succinate* (1) from *o*-xylenol, [Me_2 : OH = 1 : 2 : 4], forms colourless needles melting at 110°; (2) its isomeride from *m*-xylenol, [Me_2 : OH = 1 : 3 : 4], forms leaflets melting at 70°, and, on nitration, gives *nitroxylyl succinate*, needles, melting at 169°; (3) the corresponding ester from *p*-xylenol, [Me_2 : OH = 1 : 4 : 2], melts at 81°.

Carvacryl succinate crystallises from light petroleum in rhombic plates, melts at 37°, and boils at 264—268° under 5 mm. pressure. *Thymyl succinate* crystallises from alcohol in needles, melts at 63°, and boils at 240—250° under 20 mm. pressure. *Guaiacyl succinate* crystallises from benzene in stellate aggregates of needles, melts at 135°, and on nitration yields a *tetranitro*-derivative insoluble in all solvents.

Phenyl αβ-diethylsuccinate, $C_2H_2Et_2(CO_2Ph)_2$, prepared from the para-acid and phenol, crystallises from light petroleum in needles and melts at 107—108°; the anti-acid gives the same salt exclusively.

The following salts were prepared by heating the phenol with succinyl chloride: *α-naphthyl succinate* crystallises from benzene in small leaflets and melts at 155°; *β-naphthyl succinate* forms lustrous needles and melts at 163°. The o-, m- and p-*nitrophenyl succinates* crystallise in prisms melting at 163°, 153°, and 178° respectively.

W. A. D.

Phenyl and Benzyl Esters of Glutaric, Fumaric, Maleic, and Phthalic Acids. Carl A. Bischoff and August von Hedenström (*Ber.*, 1902, 35, 4084—4094).—*Benzyl glutarate*, prepared by heating silver glutarate and benzyl chloride at 140°, or glutaric acid with benzyl alcohol at 190°, boils at 248° under 14 mm. pressure. *Phenyl glutarate*, obtained by warming phenol with glutaric chloride, crystallises from light petroleum in sheaves of needles, melts at 54°, boils at 236·5° under 15 mm. and at 300—310° under atmospheric pressure; neither with diphenylethylenediamine nor with catechol does it give a definite condensation product.

Phenyl fumarate is converted by benzyl alcohol into benzyl fumarate, but, when heated with diphenylethylenediamine, it fails to yield any other definite product than phenol. *Phenyl maleate*, prepared by heating phenyl hydrogen maleate (*infra*) with phenol and phosphoric oxide in benzene solution, forms fan-like aggregates of leaflets, melts

at 73°, and boils at 226° under 15 mm. pressure; it is converted into the fumarate by bromine in chloroform solution, but is not affected by iodine dissolved in alcohol. When distilled at 360°, it gives rise to considerable quantities of stilbene.

Phenyl hydrogen fumarate, $CO_2H{\cdot}CH{:}CH{\cdot}CO_2Ph$, obtained by the interaction of maleic anhydride and sodium phenoxide in toluene solution at 90°, crystallises from benzene in felted needles, melts at 130° and, on distillation, gives phenol and maleic anhydride. With phosphorus pentachloride, it forms *fumaric chloride phenyl ester*, $CO_2Ph{\cdot}CH{:}CH{\cdot}COCl$, which melts at 39°, boils at 187—188° under 40 mm. pressure, and, with sodium phenoxide in benzene solution, gives phenyl fumarate. The same chloride was also obtained from fumaryl chloride and sodium phenoxide dissolved in benzene, along with the mono- and di-phenyl fumarates.

Phenyl hydrogen maleate, prepared from maleic anhydride and phenol, crystallises from a mixture of light petroleum and benzene in stellate aggregates of needles and melts at 101°. *Benzyl fumarate*, prepared by heating the acid with benzyl alcohol at 185°, or, better, by heating silver fumarate with benzyl chloride, crystallises from light petroleum in aggregates of colourless prisms, melts at 64°, and boils at 239° under 14 mm. pressure; it is also obtained when phenyl fumarate is boiled with benzyl alcohol. *Benzyl maleate*, obtained similarly, boils at 241° under 14 mm. pressure.

Phenyl phthalate melts at 73° (Vongerichten, Abstr., 1880, 473, gives 71°), boils at 250—257° under 14 mm. pressure, and fails to give a definite product when heated with diphenylethylenediamine or with catechol. *Phenyl hydrogen phthalate*, prepared by fusing phthalic anhydride with phenol and adding dilute aqueous sodium carbonate, crystallises in needles, sinters at 92°, and melts at 103°. Benzyl phthalate, which is described by Meyer (*Ber.*, 1895, 28, 1577) as melting at 42—44°, was obtained only as an oil which boiled at 277° under 15 mm., at 274° under 12 mm., pressure; it was formed by heating together benzyl alcohol and phthalic acid. *Benzyl hydrogen phthalate*, obtained along with the dibenzyl ester by the action of phthalic anhydride on benzyl alcohol, crystallises in colourless, lustrous needles, and melts at 104°. W. A. D.

Velocity of Saponification of Aryl and Benzyl Esters of Dibasic Acids. CARL A. BISCHOFF and AUGUST VON HEDENSTRÖM (*Ber.*, 1902, 35, 4094—4099. Compare this vol., i, 26).—Tables are given showing the rate of hydrolysis of the esters when boiled with sodium hydroxide in acetone solution. The benzyl radicle is most easily eliminated, and the following numbers show the percentage of benzyl ester decomposed after 5 minutes for different acids: oxalic, 100; fumaric, 41; maleic, 25; malonic, 26—21; succinic, 13—10; glutaric, 14; carbonic, 12—4. The ethyl esters are slightly less reactive, the phenyl esters being most stable; the following values are for phenyl esters under the same conditions as above: oxalic, 53; malonic, 16; fumaric, 15; maleic, 7; carbonic, 8; glutaric, 6; succinic, 5. The presence of substituted groups in the benzene nucleus in all cases increases the ease of hydrolysis. W. A. D.

Compounds of Triphenylcarbinol with Organic Bases A. E. Tschitschibabin (*Ber.*, 1902, **35**, 4007—4009. Compare Abstr., 1902, i, 395).—On mixing quinoline and triphenylcarbinol, heat is developed, and there is obtained a solid *compound*, $CPh_3·OH,C_9NH_7$, which can be recrystallised in the presence of excess of quinoline; it forms large crystals which melt at 52°. Phenylhydrazine and triphenylcarbinol similarly yield an additive *compound*,

$$CPh_3·OH,NHPh·NH_2,$$

which is more stable than the analogous quinoline derivative, and is also formed by the action of phenylhydrazine on triphenylmethyl bromide; it forms large, clear crystals which, at 86°, give a liquid containing crystals of triphenylcarbinol; it oxidises readily in the air.

With other amines, aniline, dimethylaniline, di*iso*amylamine, &c., such compounds could not be prepared. K. J. P. O.

Constitution of Nitroresorcinol. Ferdinand Henrich (*Ber.*, 1902, **35**, 4191—4195. Compare Fèvre, Abstr., 1883, 733).—Fèvre's nitroresorcinol is shown to be 1-nitro-2 : 4-dihydroxybenzene, since the product obtained on reduction is identical with the substance obtained by the action of concentrated hydrochloric acid on Kietaibl's 2-ethoxy-4-hydroxyaniline hydrochloride (Abstr., 1899, i, 345).

The melting point of the ethoxyquinone, obtained by the oxidation of the base, is 117—119°, not 107° as stated by Kietaibl.

For the preparation of nitroresorcinol, Fèvre's method is recommended, with the substitution of potassium hydroxide for the sodium compound, since the potassium derivative of the nitro-compound is very sparingly soluble. When reduced with stannous chloride, it yields the corresponding aminoresorcinol, which, when warmed with acetic anhydride at 160°, yields a *tetra-acetyl* derivative, $NAc_2·C_6H_3(OAc)_2$, melting at 106—108°. J. J. S.

Derivatives of 4-Aminoresorcinol. Ferdinand Henrich and Benno Wagner (*Ber.*, 1902, **35**, 4195—4206. Compare preceding abstract).—4-Aminoresorcinol hydrochloride has been obtained by the reduction of Weselsky's nitroresorcinol (*Annalen*, 1872, **164**, 5), *p*-benzeneazoresorcinol (Will and Pukall, Abstr., 1887, 660), or Fèvre's nitroresorcinol, and also by the hydrolysis of the corresponding ethoxy-derivative.

Tribenzoylaminoresorcinol, $NHBz·C_6H_3(OBz)_2$, obtained by the Schotten-Baumann process, crystallises in small, glistening needles melting at 172°; it is slowly hydrolysed by boiling alkalis, and the resulting solution undergoes oxidation in the same manner as the alkali solutions of the original base.

When subjected to dry distillation, it yields benzoic acid and 5-*benzoyloxy*-1-*phenylbenzoxazole*, $OBz·C_6H_3<\genfrac{}{}{0pt}{}{N}{O}>CPh$, in the form of glistening plates melting at 118·5° and readily soluble in most organic solvents. The same product is obtained when aminoresorcinol hydrochloride and benzoyl chloride are heated together. When hydrolysed

with 10 per cent. alcoholic potash, it yields 5-hydroxy-1-phenylbenzoxazole (Abstr., 1899, i, 171) which, when coupled in alkaline solution with phenyldiazonium chloride, yields a red *azo-dye*, $NPh:N\cdot C_{13}H_8O_2N$, melting at 184°.

Tri-p-nitrobenzoylaminoresorcinol, $NO_2\cdot C_6H_4\cdot NH\cdot C_6H_3(O\cdot C_6H_4\cdot NO_2)_2$, crystallises from nitrobenzene in sulphur-yellow needles melting at 266°. The corresponding *m*-nitro-derivative is colourless and melts at 231°, and the ortho-compound at 128°. When the nitro-derivatives are distilled they char and decompose.

5-Acetoxy-1-methylbenzoxazole, $OAc\cdot C_6H_3{<}{}^{N}_{O}{>}CMe$, is obtained when tetra-acetylaminoresorcinol (preceding abstract) is subjected to dry distillation. It forms long, colourless needles melting at 55°, readily soluble in most organic solvents, and, on hydrolysis with aqueous potash, yields *5-hydroxy-1-methylbenzoxazole* melting at 193°; this exhibits pronounced phenolic properties and condenses, with phenyldiazonium chloride, to *benzeneazo-5-hydroxy-1-methylbenzoxazole* in the form of golden-yellow plates melting at 91°. J. J. S.

Isomeric Ethers of Pyrogallol. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1902, 23, 700—708).—The authors describe the methylation, by means of diazomethane, of the isomeric carboxylic acids of pyrogallol. *Methyl 3 : 5-dihydroxy-4-methoxybenzenecarboxylate*, prepared from gallic acid, crystallises from benzene or water in needles and melts at 143—146°. The *acid* melts at 240—242°, whereas the isomeric 3-methoxy-compound (Vogl, Abstr., 1900, i, 697) melts at 199°. *Methyl 5-hydroxy-3 : 4-dimethoxybenzene-1-carboxylate* is formed at the same time as an oil and may also be obtained by methylating the 4-methoxy-compound. The corresponding *acid* crystallises from water in needles melting at 189—192°.

Methyl 2 : 3-dihydroxy-4-methoxybenzene-1-carboxylate, prepared in a similar manner from pyrogallolcarboxylic acid, crystallises in needles melting at 101—104°. E. F. A.

Electrolytic Preparation of Tetra-alkyldiaminobenzhydrols. F. ESCHERICH and M. MOEST (*Zeit. Elektrochem.*, 1902, 8, 849—851).—When tetramethyldiaminobenzophenone is reduced electrolytically in acid solution, a mixture of the hydrol and pinacone is produced. Using a copper cathode, the pinacone is the main product; with a nickel cathode, nearly equal parts of hydrol and pinacone are formed, whilst with cathodes of lead or mercury the hydrol predominates. Greater concentration of the sulphuric acid increases the yield of pinacone. No porous diaphragm is required, the hydrol not being oxidised by the anodic oxygen.

A solution of tetramethyldiaminobenzophenone (100 grams), 37 per cent. sulphuric acid (400 c.c.), and water (1600 c.c.), electrolysed with lead electrodes and a current density of 0·007 ampere per sq. cm., gave nearly 90 per cent. of the theoretical yield of hydrol, whilst a solution containing only 500 c.c. of water electrolysed with a copper cathode and 0·015 ampere per sq. cm. gave about 75 per cent. of the

theoretical yield of the pinacone. This substance is insoluble in alcohol or water, readily soluble in ether, it melts at 210—211°, and yields condensation products with dimethylaniline. Tetramethyldiaminodiphenylmethane in faintly acid solution is readily oxidised to the corresponding alcohol by anodic oxygen; it is therefore found that a mixture of equal molecules of tetramethyldiaminobenzophenone and diphenylmethane is converted by electrolysis into the pure benzhydrol, the whole effect of the electric current being utilised.

T. E.

Glycine Compounds of some Phenols. ALFRED EINHORN and HUGO HÜTZ (*Arch. Pharm.*, 1902, **240**, 631—640. Compare Morel, Abstr., 1900, i, 158).—Chloroacetyl derivatives of phenols, of the type $CH_2Cl \cdot CO_2R^1$, were prepared by heating chloroacetic acid with a phenol in the presence of phosphorus oxychloride and pyridine (compare Nencki, Abstr., 1894, i, 86). With primary amines of the aliphatic type, NH_2R^{11}, they react in ethereal solution to form substituted glycocollamides, $NHR^{11} \cdot CH_2 \cdot CONHR^{11}$; with secondary aliphatic amines, $NHR_2{}^{11}$, they form substituted amino-esters, $NR_2{}^{11} \cdot CH_2 \cdot CO_2R^1$. The phenols employed were phenol itself, *o*-, *m*-, and *p*-cresols, guaiacol (2-methoxyphenol), and creosol (2-methoxy-4-methylphenol). The secondary amine employed was diethylamine; in one case only, di*iso*-butylamine was used. It is only with phenol itself that primary amines were allowed to react, ethylamine and benzylamine being used. The products obtained were always oils, but crystalline salts were prepared from them.

The following new substances were obtained: *Ethylaminoacetethylamide*; the *hydrochloride* melts at 179—179·5°. *Phenyl diethylaminoacetate*; the *hydrochloride* and *hydrobromide* melt at 165° and 189° respectively. *Tolyl chloroacetates*; o-, m-, and p-, boil at 147°, 170°, and 153—154° "in a vacuum"; the last melts at 29—30°. *Tolyl diethylaminoacetates*; o- and m-*hydrochlorides* melt at 142·5° and 173·5°, o-, m-, and p-*hydrobromides* at 164°, 203°, and 133—134° respectively; o-*hydriodide* at 141·5°, and p-*picrate* at 129·5°. 2-*Methoxyphenyl diethylaminoacetate*; the *hydrochloride*, *platinichloride*, *mercurichloride*, and *hydrobromide* melt at 184—186°, 195—196°, 97—99°, and 208° respectively. 2-*Methoxyphenyl* di*iso*butylaminoacetate; the *hydriodide*, *platinichloride*, and *aurichloride* melt at 145°, 174°, and 137·5°. 2-*Methoxy*-4-*methylphenyl diethylaminoacetate*; the *hydrochloride*, *platinichloride*, and *hydriodide* melt at 176°, 124°, and 166—168°.

These amino-esters are hydrolysed very easily by dilute acids or alkalis, the phenol being liberated. They undergo this hydrolysis slowly in the juices of the intestine, and they do not themselves erode the stomach, so that they afford a very convenient form in which the phenols, especially guaiacol, can be administered in cases of tuberculosis.

2-Methoxyphenyl diethylaminoacetate hydrochloride has been introduced into medicine for this purpose under the name of *guaiasanol*.

C. F. B.

Chloraldianthranilic Acid. STANISLAUS VON NIEMENTOWSKI (*Ber.*, 1902, **35**, 3898—3900; *Bull. Acad. Sci. Cracow*, 1902, 420—421. Compare Abstr., 1896, i, 187).—*Chloraldianthranilic acid*,

$$CCl_3\cdot CH(NH\cdot C_6H_4\cdot CO_2H)_2,$$

prepared by direct condensation of chloral with anthranilic acid, forms grey, indistinct crystals, melts at 165°, and dissolves in alkalis, but not in dilute acids. Nitric acid converts it into *dinitrotrichloroethylideneanthranilic acid*, $CCl_3\cdot CH{:}N\cdot C_6H_2(NO_2)_2\cdot CO_2H$, which crystallises from alcohol in yellowish-brown, ill-defined, hexagonal tablets and melts and intumesces at 187°. T. M. L.

***iso*Nitrosobenzyl Cyanide.** M. R. ZIMMERMANN (*J. pr. Chem.*, 1902, [ii], **66**, 353—386).—Sodium *iso*nitrosobenzyl cyanide,

$$C_8H_5ON_2Na,4H_2O,$$

formed by the action of amyl or ethyl nitrite and sodium ethoxide on benzyl cyanide, crystallises from water in colourless, prismatic leaflets. *iso*Nitrosobenzyl cyanide (m. p. 129°; compare Abstr., 1888, 693; 1902, i, 541) undergoes Beckmann's reaction with phosphorus pentachloride and water, yielding phenyloxamide, and has therefore the *anti*-configuration $\begin{array}{c}Ph\cdot C\cdot CN\\ \| \\ OH\cdot N\end{array}$. When heated with quinoline at 130°, *iso*nitrosobenzyl cyanide forms a crystalline additive *compound*, $C_8H_5ON_2,C_9H_8N$, which melts at 66° and is decomposed by alkalis.

As, on liberation from its sodium derivative, *iso*nitrosobenzyl cyanide melts at first 3—4° too low, the sodium derivative, and the following derivatives prepared from it, have probably the *syn*-configuration. The *benzoate*, $CN\cdot CPh{:}NOBz$, crystallises from benzene in white prisms, melts at 138°, and is easily soluble in pyridine, insoluble in water; the *ethyl carbonate*, $CN\cdot CPh{:}NO\cdot CO_2Et$, crystallises from light petroleum in colourless needles, melts at 83°, is easily soluble in alcohol, ether, or benzene, and is decomposed by dry ammonia in ethereal solution with formation of urethane and *ammonium* iso*nitrosobenzyl cyanide*, which crystallises in yellow leaflets and is very unstable. The *methyl ether*, $CN\cdot CPh{:}NOMe$, melts at 32° and is easily soluble in light petroleum. The N-*methyl ether*, $O{<}\begin{array}{l}CPh\cdot CN\\ \mid \\ NMe\end{array}$, which is formed along with the O-methyl ether, melts at 131° and is only slightly soluble in light petroleum. The *carbonyl chloride*,

$$CN\cdot CPh{:}NO\cdot COCl,$$

which crystallises from petroleum in clusters of pale yellow needles and melts at 59°, is formed along with the *carbonate*, $CO(NO{:}CPh\cdot CN)_2$; the latter, which crystallises from benzene in nacreous leaflets and melts at 190°, is the sole product of the action of phosgene on dry sodium *iso*nitrosobenzyl cyanide at the ordinary temperature in presence of traces of water; at 100°, the reaction yields, in addition to the carbonate, two *compounds*, one of which crystallises in yellow leaflets and melts at 137·5°, and the other crystallises in white leaflets, melts at 90°, and possibly has the formula $CN\cdot CPh{:}NO\cdot CPh{:}N\cdot OH$. The *carbanilide*, $CN\cdot CPh{:}NO\cdot CO\cdot NHPh$,

which crystallises from benzene in white leaflets, becomes yellow on exposure to light and melts at 134°.

Sodium iso*nitroso*-p-*nitrobenzyl cyanide*, $C_8H_4O_3N_3Na$, crystallises in yellow leaflets or reddish-yellow needles and, on treatment with dilute acids, yields α-iso*nitroso*-p-*nitrobenzyl cyanide*, which forms yellow needles, melts at 95°, and when kept, or when heated to its melting point, changes to the *β-modification*, which melts at 164—165°. When warmed with quinoline in benzene solution, *iso*nitroso-*p*-nitrobenzyl cyanide forms an additive *compound*, which crystallises in yellow needles and melts at 172·5°. The *benzoate*,

$$NO_2\cdot C_6H_4\cdot C(CN):NOBz,$$

forms yellow needles, melts at 154°, and is easily soluble in hot alcohol, but only slightly so in cold alcohol or benzene. The *methyl ether*, $NO_2\cdot C_6H_4\cdot C(CN):NOMe$, crystallises in yellow needles and melts at 134—135°.

Sodium iso*nitroso*-p-*chlorobenzyl cyanide*, $C_8H_4ON_2ClNa$, crystallises in yellow leaflets or in colourless, prismatic leaflets containing $4H_2O$. On addition of dilute acid to a solution of the sodium compound, α-iso*Nitroso*-p-*chlorobenzyl cyanide* separates as colourless, felted, slender needles; it melts at 62°, and on keeping, or on crystallisation from petroleum, is converted into the *β-modification*, which crystallises in yellowish-green leaflets, melts at 112°, and is converted by solution in alcohol or water into the α-isomeride. The additive *compound* of quinoline and *iso*nitroso-*p*-chlorobenzyl cyanide crystallises from light petroleum in white needles and melts at 111°. The *benzoate*,

$$C_8H_4ON_2ClBz,$$

forms compact crystals, melts at 115—116°, and is soluble in petroleum or alcohol. By the action of methyl iodide on silver *iso*nitroso-*p*-chlorobenzyl cyanide, two methyl ethers are formed. The α-*methyl ether*, $O<\begin{matrix}C(C_6H_4Cl)\cdot CN \\ | \\ NMe\end{matrix}$, crystallises from a mixture of benzene and petroleum in slender needles, melts at 120°, is insoluble in light petroleum, and forms an additive *compound* with hydrogen chloride in benzene solution. The *β-methyl ether*,

$$C_6H_4Cl\cdot C(CN):N\cdot OMe,$$

crystallises in colourless needles, melts at 68—69°, and is soluble in light petroleum.

The mother liquor from the preparation of sodium *iso*nitroso-*p*-chlorobenzyl cyanide contains iso*nitroso*-p-*chlorophenylacetamide*,

$$C_6H_4Cl\cdot C(CO\cdot NH_2):N\cdot OH;$$

on acidification, this is obtained in a labile modification which melts at 97°, and when kept changes into the stable form melting at 150°.

o-Chlorobenzyl cyanide melts at 24° and boils at 251° under 756 mm. pressure (compare Mehner, Abstr., 1901, i, 208). iso*Nitroso*-o-*chlorobenzyl cyanide* is obtained in two modifications, of which the α- melts at 70—88° and is converted, by crystallisation from benzene, into the β-form which melts at 126°. The quinoline additive *compound* crystallises in slender, white needles and melts at 76°. The *benzoate* crystallises in white needles, melts at 105°, and is moderately soluble in benzene but less so in light petroleum. The α-*methyl ether*,

$$O<\begin{matrix}C(C_6H_4Cl)\cdot CN \\ | \\ NMe\end{matrix} \quad (?),$$

crystallises in rhombic prisms, melts at 89°, and is insoluble in light petroleum. The *β-methyl ether*, $C_6H_4Cl\cdot C(CN)\vdots N\cdot OMe$ (?), crystallises in colourless, rhombic prisms, melts at 37°, and is easily soluble in light petroleum.

These *iso*nitroso-cyanides do not undergo hydrolysis, and, with the exception of *iso*nitrosobenzyl cyanide, they do not exhibit the Beckmann reaction. The author considers the α-modifications to have the *syn*-, the β-modifications the *anti*-configuration.

The action of nitrous acid on the *iso*nitroso-cyanides results in the formation of the corresponding benzoyl cyanides. *p*-Nitrobenzoyl cyanide, $NO_2\cdot C_6H_4\cdot CO\cdot CN$, crystallises in quadratic, yellow leaflets, melts at 116·5° (compare Haussknecht, Abstr., 1889, 506), and is easily soluble in ether or warm benzene. Along with o-*chlorobenzoyl cyanide*, which crystallises in colourless, rhombic plates and melts at 35°, there is formed a small quantity of a *product* (azoperoxide?) melting and evolving gas at 116°. *iso*Nitroso-*p*-chlorobenzyl cyanide yields p-*chlorobenzoyl cyanide*, which crystallises in colourless, quadratic leaflets, melts at 40°, and is easily soluble in the usual organic solvents, and a small quantity of a *product* (azoperoxide?) which melts and evolves gas at 134°. G. Y.

Interpretation of the Action of Ferric Chloride on Salicylic Acid, Methyl Salicylate, Salicylaldehyde, and certain other Phenolic Compounds. A. DESMOULIÈRE (*J. Pharm. Chim.*, 1902, [vi], **16**, 241—245).—The decolorisation of aqueous solutions of methyl salicylate and salicylaldehyde, coloured by ferric chloride, on shaking with chloroform, ether, ethyl acetate, benzene, or light petroleum, depends on the instability of the ferric compounds, and on the relative solubility of the phenolic compound in water and the organic solvent. Whilst salicylic acid is not extracted by any of these solvents, phenol is extracted by ether and ethyl acetate, partially by chloroform and benzene, but not by light petroleum, and resorcinol is extracted by ether or ethyl acetate, but not by chloroform, benzene, or light petroleum. G. D. L.

Fission of Acid Anhydrides by Alcohols and Alkyloxides and the Mechanism of Esterification. ROBERT KAHN (*Ber.*, 1902, **35**, 3857—3883).—3-Nitrophthalic anhydride is formed quantitatively on heating the acid in a bath of *n*-propyl benzoate (b. p. 229·5°) until water ceases to be evolved (compare Bogert and Boroschek, Abstr., 1902, i, 98, and Lipschitz, Abstr., 1901, i, 32).

The β-ester, obtained by the action of methyl alcohol on 3-nitrophthalic acid in presence of hydrochloric or sulphuric acid, is shown to have the structure $[CO_2Me : CO_2H : NO_2 = 1 : 2 : 3]$ by the following facts. When dissolved in ammonia of sp. gr. 0·916, it gives 3 : 1-*nitrophthalamic acid*, $[CO_2\cdot NH_2 : CO_2H : NO_2 = 1 : 2 : 3]$, which is moderately soluble in warm water and crystallises in lustrous, thick plates; it does not melt at a definite temperature and is hydrolysed by acetic acid or by prolonged boiling with water.

The amic acid is converted by alkaline hypobromite into 6-nitro-2-aminobenzoic acid (compare Kahn, Abstr., 1902, i, 228), which has an intensely sweet taste, and, on boiling with sulphuric acid in methyl alcoholic solution, gives *m*-nitroaniline. On diazotising the amino-acid in dilute sulphuric acid and decomposing by heat, the carboxyl group is eliminated and *m*-nitrophenol obtained.

The α-methyl ester, $[CO_2H : CO_2Me : NO_2 = 1 : 2 : 3]$, is not acted on when heated with aqueous ammonia at 100° for 5 hours, but at 150° is completely hydrolysed.

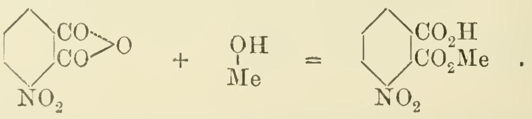
3-Nitrophthalimide is best prepared by passing dry ammonia gas into the fused anhydride; it gives a crystalline *potassium* derivative, $C_8H_3O_4N_2K$, and is converted by alkali hydrolysis into 3 : 1-nitrophthalamic acid, and not the isomeric compound,

$$[CO_2H : CO{\cdot}NH_2 : NO_2 = 1 : 2 : 3],$$

as stated by Bogert and Boroschek.

In attempting to obtain a method of separating the α- and β-3-nitrophthalic acid esters, it was found that the β-methyl ester, when heated for 7 hours on the water-bath with methyl alcohol and sulphuric acid, gave only 2·9 per cent. of the normal ester, and that the α-ester, under similar conditions, gave 85 per cent. of the same compound, 15 per cent. remaining unchanged. In the following cases, when a mixture of the α- and β-acid esters is formed by the action of alcohol or alkyloxide on the anhydride of the acid, they can be separated quantitatively by taking advantage of the greater solubility of the β-salt in water.

When 3-nitrophthalic anhydride is heated for 8 hours with anhydrous methyl alcohol, it gives 83 per cent. of α-ester, 6·5 per cent. of β-ester, and 10·4 per cent. remains unchanged; as stated by Wegscheider, the "stronger" carboxyl group is here esterified, but the author assigns the fact to a different cause. The alcohol initially causes a fission of that bond (indicated by a dotted line) between CO and O, which is not protected by the influence of the adjacent nitro-group:



For a similar reason, the partial hydrolysis of the diethyl salt will give the α-ester, and in both cases the result is considered as being independent of the relative strengths of the carboxyl groups.

With 3-nitrophthalic anhydride dissolved in absolute methyl alcohol, sodium methoxide gives 60—62 per cent. of α-ester and 23—25 per cent. of β-ester, the remainder of the acid being unchanged; the result is practically the same when methyl alcoholic potassium hydroxide is employed, and this fact is used as an argument against Wegscheider's view that the β-ester is the normal product and that the α-acid is formed by a process of catalysis. The formation of the two esters may be due to the production initially of additive compounds, but attempts to isolate these were unsuccessful; the large proportion of β-ester formed is considered by the author as due to the methoxide reacting

either as a compound of ·OR and Me, or as if composed of R and ·OMe. W. A. D.

Action of Phthalic Chloride on Arylsulphinates, Arylthiosulphonates, and Arylmercaptides. JULIUS TROEGER and VICTOR HORNUNG (*J. pr. Chem.*, 1902, [ii], 66, 345—352. Compare Abstr., 1899, i, 905).—The action of phthalic chloride on potassium benzenethiosulphonate and *p*-toluenethiosulphonate in alcoholic solution leads to the formation of the corresponding disulphides, which are decomposed by the alcohol into a mixture of mono- and tri-sulphides.

Bisphenylsulphone-phthalide, $C_6H_4<\overset{C(SO_2Ph)_2}{\underset{CO}{}}>O$, formed by the action of phthalic chloride on sodium benzenesulphinate, crystallises from alcohol in needles and melts at 193—194°.

Bis-p-*tolylsulphone-phthalide*, formed from sodium *p*-toluenesulphinate, crystallises in glistening needles and melts at 239°.

Bisphenylthio-phthalide, $C_6H_4<\overset{C(SPh)_2}{\underset{CO}{}}>O$, formed by the action of phthalic chloride on lead phenylmercaptide, crystallises from alcohol in glistening leaflets, melts at 84—85°, and is oxidised by potassium permanganate to bisphenylsulphone-phthalide. The action of phthalic chloride on sodium β-naphthylmercaptide leads to the formation of β-naphthyl disulphide and *bis-β-naphthylthio-phthalide*, which crystallises from alcohol in needles and melts at 153—154°. G. Y.

Phenolphthaleïn as Indicator. OTTO SCHMATOLLA (*Ber.*, 1902, 35, 3905—3907. Compare R. Hirsch, Abstr., 1902, ii, 690).—The red compounds of phenolphthalein are more or less decolorised by dehydration; the compounds with alkali hydroxides are colourless in strong alkali solution, but become strongly coloured on dilution; similarly, in alcoholic solution, alkali hydroxides yield only pale red solutions, but these become intensely red on dilution with water. The red compounds formed by alkali hydrogen carbonates are still more easily decolorised by the addition of either alcohol or normal salts in dilute solutions. T. M. L.

The Phthaleins. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1902, 23, 709—711).—On methylating fluorescein by means of diazomethane, practically only the quinonoid diether is formed, whereas in alkaline solution, using methyl iodide, the lactone diether is the chief product. Phenolphthalein and diazomethane, however, gave the lactone diether, the methylation proceeding as in alkaline solution.

E. F. A.

Pentabenzoyltannic Acid. VOURNASOS (*J. Pharm. Chim.*, 1902, [vi], 16, 245—250).—*Pentabenzoyltannic acid*, produced by heating together tannic acid and benzoyl chloride, forms slender, silky needles melting at 140°, is insoluble in alcohol or water, soluble in acetone, ether, or benzene, and, on hydrolysis, is resolved into benzoic and tannic acids; digestion with alkali hydroxides or concentrated mineral acids gives gallic acid. G. D. L.

Usnic Acid. Oskar Widman (*Annalen*, 1902, **324**, 139—200. Compare Abstr., 1900, i, 235, 347; Paternò, Abstr., 1900, i, 662; Salkowski, Abstr., 1901, i, 152).—The communication commences with a critical survey of work already published.

The behaviour of decarbousnic acid towards ammonia agrees with the author's formula, $CHAc\cdot CH{:}C{<}{\substack{O-CO \\ C(OH)}}{\geq}C\cdot CH(C_8H_{11})\cdot CO_2H$, which represents the compound as being a lactonic acid; it forms a *diammonium* salt, $C_{17}H_{16}O_6(NH_4)_2$, which readily loses ammonia and passes into the *monoammonium* salt, $C_{17}H_{17}O_6\cdot NH_4$; the latter derivative decomposes at 120° and readily dissolves in warm alcohol, but is only partially soluble in water.

d- and *l*-syn-*Usnic acid oxime*, $C_{18}H_{16}O_6{:}NOH$, prepared by treating the amorphous product of the action of hydroxylamine hydrochloride on usnic acid with a 3 per cent. solution of hydrogen chloride in methyl or ethyl alcohol, crystallises from the latter solvent in yellow prisms which sinter at 200° and decompose at 240—241°; it has $[\alpha]_D$ +495·7° at 14°. Alcoholic acetic acid also induces the transformation of the amorphous oxime into the crystalline compound; the *acetyl* derivative of the latter substance crystallises from acetic anhydride in leaflets melting at 194°.

The *anhydride*, $C_{17}H_{15}O_4{<}{\substack{N- \\ CO}}{>}O$, of *i*-usnic acid oxime results from the interaction of usnic acid and hydroxylamine acetate in benzene-alcohol solution; it crystallises from glacial acetic acid in yellow cubes or plates, melts at 235°, dissolves in cold alkaline solution, and develops a brown coloration with alcoholic ferric chloride. *i*-anti*Usnic acid oxime*, $C_{18}H_{16}O_6{:}NOH$, isolated from the mother liquors of the crystallisation of the preceding compound, is a sparingly soluble, yellow powder decomposing at 208°; it is readily converted into the anhydride by warming with acetic anhydride.

In the condensation of hydroxylamine acetate with *d*-usnic acid, the corresponding *d*-anhydride is produced, and the mother liquors in this case contain *d*-anti*usnic acid oxime*; this substance separates in pale yellow or white crystals melting at 217—220°.

The iso*anhydride*, $C_{18}H_{15}O_6N$, of *d*-usnic acid oxime, prepared by treating the crude product of the interaction of *d*-usnic acid and hydroxylamine acetate with cold potassium carbonate solution and acidifying the filtrate with acetic acid and crystallising the precipitate thus obtained from dilute acetic acid, separates in well-defined, lustrous cubes with hemihedral planes, and decomposes at 255°.

The *d*-anhydride, when subjected to the Beckmann transformation, yields an *isomeride* which crystallises from methyl alcohol in slender needles and decomposes at 255°. This derivative is not readily attacked by hydrolytic agents, and, when heated at 125° with alcoholic sulphuric acid, it furnishes a tarry product and a volatile base, probably methylamine. The formula

$$\begin{array}{l} NHMe\cdot CO\cdot \overset{}{C}{=\!=}C\cdot O\cdot CO \\ \qquad\qquad\quad\ | \qquad\ \ | \qquad\ | \\ \qquad\qquad\ CO\cdot O\cdot C{=}C\cdot CH(C_8H_{11})\cdot CO_2H \end{array}$$

represents the relationships of this product of the Beckmann change to the isomeric *d*-anhydride and allied substances.

Usnolic acid, $C_{18}H_{16}O_7$ (compare Stenhouse and Groves, Trans., 1881, **39**, 234; Paternò, Abstr., 1882, 1080; and Hesse, Abstr., 1895, i 298), decomposes indefinitely between 210° and 240°; it is a dibasic acid yielding, however, an acid sodium salt and the *methyl* ester, $C_{17}H_{15}O_5 \cdot CO_2Me$; the latter derivative crystallises from methyl alcohol in pale yellow needles and melts at 202°. The *oxime*, $OH \cdot N:C_{17}H_{15}O_4 \cdot CO_2Me$, crystallises in slender needles, melts at 220°, and forms an *acetyl* derivative, $OAc \cdot N:C_{17}H_{15}O_4 \cdot CO_2Me$, separating in pale yellow needles, insoluble in potassium hydroxide solution, and melting at 184°.

Ethyl usnolate, $C_{17}H_{15}O_5 \cdot CO_2Et$, prepared by heating usnolic acid with alcoholic hydrogen chloride, crystallises in soft, pale yellow needles melting at 175—176°; its *oxime* crystallises from alcohol and melts at 177—178°.

When warmed with excess of aniline, usnolic acid yields the anilide, $C_{23}H_{23}O_5N$, of decarbousnic acid; this product crystallises from alcohol in pale yellow needles and melts at 235—236°.

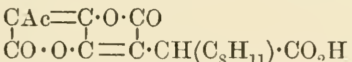
When warmed with concentrated sulphuric acid, decarbousnic acid yields *decarbousnole*; this substance crystallises in yellow needles or hexagonal plates and melts at 209°.

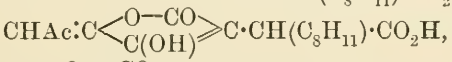
Decarbousnole is a monobasic acid; its *sodium* salt,

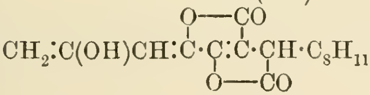
$$C_{17}H_{15}O_5Na,3H_2O,$$

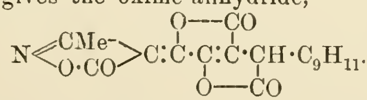
obtained by dissolving the compound in sodium carbonate solution, crystallises in yellow needles.

Acetyldecarbousnole, $C_{17}H_{15}O_4 \cdot OAc$, obtained by boiling the preceding acid with acetic anhydride, crystallises from methyl alcohol in orange-coloured prisms melting at 130—135°; it is insoluble in sodium carbonate solution, but is slowly hydrolysed by cold aqueous potassium hydroxide.

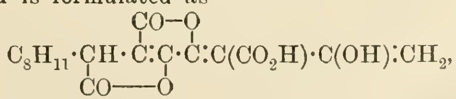
The following formulæ,  ,



and  are suggested for usnic acid, decarbousnic acid, and decarbousnole respectively. The first of these substances gives the oxime-anhydride,



Usnolic acid is formulated as



and constitutional formulæ for its methyl ester and the acetyl oximino-derivative of methyl usnolate are also indicated. The constitution of the colourless and yellow salts of decarbousnic acid is likewise discussed at considerable length. G. T. M.

Cetraric Acid. O. Simon (*Arch. Pharm.*, 1902, **240**, 521—560. Compare Hilger and Buchner, Abstr., 1890, 600; Hesse, Abstr., 1898, i, 534).—Cetraric acid was prepared by extracting Iceland moss with alcohol (after it had been extracted already with ether), evaporating the extract, extracting the residue with ether (which removes fumaric acid), crystallising what remained from alcohol, and purifying it further by dissolving it in cold aqueous sodium carbonate and precipitating it at once from the solution by means of hydrochloric acid.

Cetraric acid, $C_{19}H_{15}O_8\cdot OMe$, decomposes at 200—230°, is optically inactive, reduces Fehling's solution, gives the iodoform reaction, and when titrated with an alkali, it reacts like a dibasic acid; its *calcium* and *ammonium* salts have a corresponding composition. The normal potassium and sodium salts could not be obtained, perhaps owing to their great solubility, whereas the *potassium hydrogen* and *sodium hydrogen* salts were obtained with ease owing to their comparative insolubility. The acid forms *compounds* also with 1 mol. of pyridine, of picoline, and of quinoline; these melt and decompose at 140°, 127—134°, and 153—155° respectively. A *phenylimide*, $NPh\colon C_{19}H_{15}O_7\cdot OMe$, a p-*tolylimide*, $C_{20}H_{18}O_8\colon N\cdot C_6H_4Me$, and a *methylimide*, $C_{20}H_{18}O_8\colon NMe$, the last decomposing above 100°, were prepared; all these are yellow. The *methyl ester*, $C_{20}H_{17}MeO_9$, melts at 158—160° and forms a yellow *phenylimide* and a *dibenzoyl* derivative which melt at 180—182° and 183—184° respectively. Cetraric acid reacts with diazobenzene hydroxide, forming a red *compound* which seems to have the composition $N_2Ph\cdot C_{18}H_{14}O_6\cdot OMe$, a carboxyl group having been displaced; this substance yields a red *monoacetyl* derivative melting at 193—195°. With phenylhydrazine, it forms a *compound*, $NHPh\cdot N\colon C_{20}H_{18}O_8,NH_2\cdot NHPh$, which loses the extra molecule of phenylhydrazine when it is crystallised from alcohol or chloroform, leaving a yellow *derivative* that decomposes at 190—240°; with *p*-bromophenylhydrazine, it forms a yellow *derivative*,

$$C_{20}H_{18}O_8\colon N\cdot NH\cdot C_6H_4Br.$$

With semicarbazide, it forms a semicarbazone,

$$C_{20}H_{18}O_8\colon N\cdot NH\cdot CO\cdot NH_2.$$

When cetraric acid is heated with zinc powder and aqueous sodium hydroxide (Boehm, Abstr., 1899, i, 32), it yields products of which only orcinol could be identified with certainty. *Orcinol dibenzoate*, $C_7H_6Bz_2O_2$, melts at 87°.

Fumaric acid is not a product of the decomposition of cetraric acid; the latter substance is not affected by boiling alcoholic potassium hydroxide. An acid which is probably identical with Hesse's protocetraric acid can be obtained, however, by extracting Iceland moss with ether. Fumaric acid appears to be precipitated along with this acid in a form such that it cannot be extracted with water from the residue of the ethereal extract. This product is, however, hardly a definite compound, for its solution in an aqueous alkali carbonate, when acidified with hydrochloric acid and again extracted with ether, yields a mixture from which fumaric acid is removed by boiling water. By crystallising the final residue from alcohol, an *acid* is obtained which has approximately the composition of Hesse's protocetraric acid;

the formula $C_{19}H_{16}O_9$ is assigned to it, and cetraric acid, which is identical with Merck's "cetrarin," is possibly its methyl derivative.

C. F. B.

Electrochemical Reduction of Ketones. Karl Elbs and K. Brand (*Zeit. Elektrochem.*, 1902, 8, 783—788).—The ketones are dissolved in a solution of sodium hydroxide or acetate containing alcohol when necessary. A porous earthenware diaphragm is used and the electrodes are of lead, the cathode being prepared in the way described by Tafel (Abstr., 1900, ii, 588). Acetone gives a moderate yield of *iso*propyl alcohol and a very small quantity of pinacone.

Methyl ethyl ketone behaves in a similar way, but the yields are even worse. Acetophenone gives a mixture of phenylmethylcarbinol and acetophenonepinacone.

Benzophenone yields about 90 per cent. of the theoretical quantity of benzhydrol.

Phenyl *p*-tolyl ketone gives 80 to 90 per cent. of the theoretical quantity of the corresponding alcohol.

Phenyl *m*-xylyl ketone is also reduced to the alcohol; the product, however, is a liquid. Phenyl α-naphthyl ketone gives a fairly good yield of the corresponding carbinol, melting at 86·5°.

p-Hydroxybenzophenone formed a black deposit on the cathode which prevented the reduction; its benzoate was, however, reduced to the carbinol, a substance which crystallises from alcohol in slender needles melting at 112—113°. Tetramethyl-*p*-diaminobenzophenone yields about 60 per cent. of the theoretical quantity of the alcohol. Dibenzyl ketone yielded an oily substance, the nature of which was not determined.

A similar set of experiments was carried out, using sulphuric acid in place of sodium hydroxide. Acetone (300 grams) yielded *iso*propyl alcohol (120 grams) and pinacone hydrate (60 grams). Methyl ethyl ketone gave *sec*-butyl alcohol and methylethylpinacone (m. p. 50°). The yields were poor. Acetophenone gives about equal quantities of phenylmethylcarbinol and acetophenonepinacone. Benzophenone yields β-benzpinacolin when high current densities are used and the liquid kept warm, whilst with very low current densities and temperatures (0° to 2°) benzhydrol and diphenylmethane are the chief products. From a warm solution of phosphoric acid in acetone, however, α-benzoylpinacolin is obtained.

Phenyl-*p*-tolyl ketone yields the corresponding carbinol and pinacone, the latter being the principal product at higher temperatures and current densities. Phenyl-*m*-xylyl ketone behaves in the same way, whilst phenyl-α-naphthyl ketone yields phenyl-α-naphthyl-β-pinacolin. *p*-Ethoxybenzophenone gives a similar result, whilst *p*-hydroxybenzophenone and phthalyl-*p*-aminobenzophenone yield the corresponding pinacones melting at 80° and 140° respectively.

T. E.

Oxidation of the Oximes. Eugen Bamberger and Richard Seligman (*Ber.*, 1902, 35, 3884—3886).—When acetophenoneoxime or

phenylethylketoxime is boiled for 3—5 seconds with a neutralised solution of Caro's acid, an ethereal extract of the product gives, with ferric chloride, an intense brownish-red coloration, indicating the formation of a nitronic acid (*iso*nitro-compound); if the boiling is continued, the reaction is no longer given, owing to the conversion of the nitronic acid into a nitro-compound. The oxidation of oximes therefore takes place according to the scheme

$$>C:N\cdot OH \longrightarrow >C:NO\cdot OH \longrightarrow >CH\cdot NO_2 .$$

Phenylmethylnitromethane, $CHMePh\cdot NO_2$, prepared from acetophenoneoxime, boils at 115—115·5° (corr.) under 11 mm. pressure.

W. A. D.

Cyclic Ketones from Chloroform and Phenols. II. KARL AUWERS and G. KEIL (*Ber.*, 1902, **35**, 4207—4217. Compare Abstr., 1902, i, 218).—The proportion of the chlorinated cyclic ketones obtained by the action of chloroform on phenols varies according to the manner in which Reimer's reaction is performed.

1-Methyl-1-dichloromethyl-4-ketodihydrobenzene (*loc. cit.*) forms a *semicarbazone*, which crystallises from dilute alcohol in white prisms and melts at 184°, a p-*bromophenylhydrazone*, which crystallises in small, yellow prisms and melts at 96°, and a p-*nitrophenylhydrazone*, which crystallises in reddish-yellow leaflets and prisms and, when slowly heated, melts and decomposes at 180°.

An eight per cent. yield of 1-*methyl*-1-*dichloromethyl*-2-*ketodihydrobenzene* is obtained from *o*-cresol, chloroform, and alkali when the presence of an excess of the last is avoided during the course of the reaction; it crystallises in large, transparent plates and prisms, softens at 30°, melts at 33°, and forms a *semicarbazone* which crystallises in small needles and melts at 198°. The corresponding chlorinated ketone from *m*-cresol was not obtained. The *semicarbazone* of 1 : 2-dimethyl-1-dichloromethyl-4-ketodihydrobenzene (Abstr., 1900, i, 160) crystallises in lustrous, white prisms which melt at 212°, the *semicarbazone* of 1 : 3-dimethyl-1-dichloromethyl-4-ketodihydrobenzene crystallises in small, slender, lustrous, white needles and melts at 182—186°. The *semicarbazone* of 1 : 2 : 5-trimethyl-1-dichloromethyl-4-ketodihydrobenzene was obtained as a mass of slender, white crystals which melted at 192°.

R. H. P.

Alkylidenedeoxybenzoins. AUGUST KLAGES and F. TETZNER (*Ber.*, 1902, **35**, 3965—3972. Compare Klages and Knoevenagel, Abstr., 1893, i, 350, 353, and Stobbe and Niedenzu, *ibid.*, 1902, i, 103).—p-*Methyl-a-chlorobenzyldeoxybenzoin*,

$$C_6H_4Me\cdot CHCl\cdot CHPh\cdot COPh,$$

obtained by the condensation of ethereal solutions of p-tolualdehyde and deoxybenzoin in the presence of hydrogen chloride, crystallises from alcohol or acetic acid in small, colourless needles melting at 156°. When shaken with aqueous potassium hydroxide, it is converted into a mixture of two isomeric p-*methylbenzylidenedeoxybenzoins*,

$$C_6H_4Me\cdot CH:CPh\cdot COPh;$$

the α-compound crystallises from alcohol in glistening needles melting at 95°, and the β-derivative, which is somewhat more soluble in alcohol,

melts at 78°. Both yield the same *phenylhydrazone* melting at 187°. When distilled under reduced pressure, the chloro-derivative yields benzoyl chloride and *p*-methylstilbene melting at 117°.

p-iso*Propyl-a-chlorobenzyldeoxybenzoin* crystallises in glistening plates melting at 142—143°.

a-p-iso*Propylbenzylidenedeoxybenzoin* melts at 103—104°, and the isomeric β-compound, which is more readily soluble in alcohol, melts at 65°. Hydrogen chloride readily combines with the a-compound, but first transforms the β-modification into the a-isomeride.

iso*Propylbenzamarone*, $C_3H_7\cdot C_6H_4\cdot CH(CHPh\cdot COPh)_2$, crystallises from hot acetic acid in colourless needles melting at 225°.

o-a-*Dichlorobenzyldeoxybenzoin*, $C_6H_4Cl\cdot CHCl\cdot CHPh\cdot COPh$, is sparingly soluble in alcohol and melts at 159°; it yields two isomeric o-*chlorobenzylidenedeoxybenzoins*, the a-compound melting at 113° and the β- at 92°. The *phenylhydrazone* melts at 131°. o-*Chlorostilbene* crystallises in needles and melts at 40°; its dibromide melts at 176°.

p-*Methoxy-a-chlorobenzyldeoxybenzoin* crystallises from benzene in colourless needles melting at 144°. When distilled under diminished pressure, it yields *p*-methoxybenzylidenedeoxybenzoin and not *p*-methoxystilbene. a- and β-p-*Methoxybenzylidenedeoxybenzoins* melt respectively at 113° and 85°; the *oxime* of the a-compound melts at 155°. p-*Methoxybenzamarone* melts at 233—234°.

3 : 4-*Dimethoxy-a-chlorobenzyldeoxybenzoin* melts at 164°, it does not yield a benzylidene derivative with alkalis, and is not decomposed into a stilbene derivative when distilled. Piperonaldehyde and deoxybenzoin yield a product melting at 203—204°. J. J. S.

3 : 5-Dimethoxybenzoylacetophenone. Carl Bülow and Gustav Riess (*Ber.*, 1902, **35**, 3900—3905).—3 : 5-Dimethoxybenzoic acid (dimethyl-a-resorcylic acid), prepared by methylating dihydroxybenzoic acid with methyl sulphate, sublimes without decomposition in long, white needles and melts at 180—181° (Meyer, Abstr., 1888, 148, gives 175—176°). The *methyl* ester, $C_{10}H_{12}O_4$, crystallises from dilute alcohol in large, four-sided tablets and melts at 41° (Meyer gave 81°, *loc. cit.*)

3 : 5-*Dimethoxybenzoylacetophenone*, $C_6H_3(OMe)_2\cdot CO\cdot CH_2Bz$, prepared by condensing the methyl ether with acetophenone in presence of metallic sodium, crystallises from dilute alcohol, acetic acid, or ether in minute needles and melts at 75°; the *copper* salt crystallises from benzene in glistening, moss-green needles, which melt and decompose at 190° and have the composition $C_{34}H_{30}O_8Cu,C_6H_6$.

3-*Phenyl*-5-*dimethoxyphenyl*iso*oxazole*, $\begin{array}{l}CPh\cdot CH \\ \| \\ N\text{———}O\end{array}\!\!>C\cdot C_6H_3(OMe)_2$, prepared by the action of hydroxylamine on the preceding compound, crystallises from dilute alcohol in long, glistening, colourless needles and melts at 82°.

Benzeneazodimethoxybenzoylacetophenone,

$$C_6H_3(OMe)_2\cdot CO\cdot CHBz\cdot N\colon NPh,$$

crystallises from alcohol and melts at 108°. T. M. L.

Action of Aniline on Tetrabromo-*o*-Benzoquinone. C. Loring Jackson and H. C. Porter (*Ber.*, 1902, 35, 3851—3854).—Details are given for preparing *dianilinodibromo*-o-*benzoquinone*, $C_6O_2Br_2(NHPh)_2$, by the action of aniline on tetrabromo-*o*-benzoquinone; it crystallises from a mixture of benzene and light petroleum in reddish-purple needles, melts at 160°, and combines with aniline to form the *additive* compound, $C_6O_2Br_2(NHPh)_2,NH_2Ph$, which crystallises in brown, slender needles melting at 123° and is easily decomposed by acids or by heating its solution in benzene at 50—60°. The *additive* compound, $C_6O_2Br_2(NHPh)_2,EtOH$, obtained by crystallising dianilinodibromo-*o*-benzoquinone from alcohol, can be recrystallised from warm benzene, but gradually loses alcohol in solution at 60°; it melts and decomposes at about 143°, and the analogous methyl alcohol *derivative* at 144—145°. *Dianilinobromo*-p-*benzoquinone anil*, $NPh{:}C_6HOBr(NHPh)_2$, obtained by heating any of the preceding compounds with aniline hydrobromide and alcohol, crystallises from a mixture of methyl alcohol and benzene in rhombic plates and melts at 173°. W. A. D.

Naphthaquinonediketohydrindene. Wilhelm Stadler (*Ber.*, 1902, 35, 3957—3964).—Liebermann and Lanser's bromonaphthaquinonediketohydrindene (Abstr., 1901, i, 467) gives blue *sodium* and *ammonium* salts, and, although containing four carbonyl groups, yields only a *monoxime* melting at 233°. A point in favour of the ketonic as against the enolic constitution is the non-formation of acetyl derivatives.

Anilinonaphthaquinonedik-tohydrindene, $C_{25}H_{15}O_4N$, obtained when an alcoholic solution of the bromo-derivative is boiled with aniline, forms reddish-brown needles insoluble in alcohol or benzene. 1-*Phenyl*-2 : 3-*benzoylene*-4 : 5-*phthalylpyrrole*, $C_6H_4{<}\begin{matrix}CO{\cdot}C{\cdot}NPh{\cdot}C{\cdot}C_6H_4\\ CO{\cdot}C\text{———}C{\cdot}CO\end{matrix}$, is formed when aniline is heated with an acetic acid solution of the bromo-derivative; it crystallises from nitrobenzene and sublimes in red needles soluble in concentrated sulphuric acid.

When the bromo-derivative is boiled with alcoholic potash, the product is 2-*diketohydrindeneindone*-3-*carboxylic acid*,

$$\begin{matrix}C(CO_2H)\\ C_6H_4{\cdot}CO\end{matrix}{>}C{\cdot}CH{<}\begin{matrix}CO\\ CO\end{matrix}{>}C_6H_4,$$

and not the hydroxy-derivative which might be expected. It crystallises in pyramids, melts at 242°, cannot be acetylated, and dissolves readily in hydrogen carbonate solution. Bromine, in carbon bisulphide solution, yields 2-*bromodiketohydrindeneindone*-3-*carboxylic acid*, crystallising in yellow needles and melting at 234°, and when this is treated with cold alkalis or acetic acid it yields bisdiketohydrindene (Abstr., 1894, i, 38).

2-*Diketohydrindene*-3-*ethoxyhydrindone*-3-*carboxylolactone*,

$$C_6H_4{<}\begin{matrix}C(OEt)\text{—}CO{\cdot}O\\ \text{—}CO\text{—}\end{matrix}{>}CH{\cdot}C{<}\begin{matrix}CO\\ CO\end{matrix}{>}C_6H_4,$$

obtained by shaking the bromo-acid with absolute alcohol, crystallises from chloroform in rhombic plates melting at 138°; the corresponding

methoxy-derivative melts at 198°. Both compounds, when warmed with alkali, yield diketohydrindeneindonecarboxylic acid; with hydriodic acid and red phosphorus, they give bisdiketohydrindene, and when heated at about 280°, dihydroxynaphthacenequinone (*iso*diphthalylethane) is produced (Abstr., 1897, i, 245).

2-Diketohydrindene-2-bromo-3-methoxyhydrindone-3-carboxylolactone melts at 198° and the *ethoxy*-compound at 211°.

Bromonaphthaquinonebromodiketohydrindene, $C_{19}H_8O_4Br_2$, crystallises in yellow plates and melts at 225°. J. J. S.

Autoxidation of Anthragallol. II. MAX BAMBERGER and A. PRAETORIUS (*Monatsh.*, 1902, **23**, 688—699).—The authors have further examined the products of oxidation mentioned in the first paper (Abstr., 1901, i, 730) and find that the sulphur-yellow compound has the formula $C_{12}H_8O_5$, that of the silver salt being $C_{12}H_6O_5Ag_2$. The methyl derivative, when pure, melts at 144°. The substance is found to be identical with the hydroxy-α-naphthaquinoneacetic acid prepared by Liebermann from ethyl bromonaphthaquinonemalonate. The authors discuss the changes involved in the oxidation.

E. F. A.

Syntheses in the Camphor Group with Magnesium Powder. SIGNE M. MALMGREN (*Ber.*, 1902, **35**, 3910—3912).—α-Bromocamphor combines with magnesium to form a compound which interacts with ketones to form tertiary alcohols.

*Hydroxy*iso*propylcamphor*, $C_8H_{14}<\begin{matrix}CH\cdot CMe_2\cdot OH\\ |\\ CO\end{matrix}$, prepared by condensation with acetone, crystallises from light petroleum in large, colourless prisms and melts at 88° (uncorr.); when acted on by dilute sulphuric acid, it loses H_2O and yields an unsaturated compound, $C_{13}H_{20}O$. The *diphenyl* compound, $C_8H_{14}<\begin{matrix}CH\cdot CPh_2\cdot OH\\ |\\ CO\end{matrix}$, prepared by condensation with benzophenone, separates from light petroleum in large, colourless crystals and melts at 122·5° (uncorr.). Condensation with camphor yields the *compound*

$$C_8H_{14}<\begin{matrix}CH & - & C(OH)\\ | & & |\\ CO & & CH_2 -\end{matrix}>C_8H_{14},$$

which crystallises from light petroleum in long, colourless, prismatic needles and melts at 160° (uncorr.). T. M. L.

Study of Terpenes and Ethereal Oils. Transformation of Cyclic Ketones into Alkamines and Cyclic Bases not containing Oxygen. OTTO WALLACH (*Annalen*, 1902, **324**, 281—309. Compare Abstr., 1900, i, 44, 589).—Piperidine may be produced by reducing 2-piperidone with sodium and amyl alcohol, the keto-base itself being obtained by the transformation of *cyclo*pentanoneoxime with dilute sulphuric acid. By a similar series of changes, 3-methyl*cyclo*pentanoneoxime yields a mixture of methylpiperidines. A *base*, $C_{10}H_{20}NH$, obtained from thujamenthone*iso*oxime, boils at 200—203° and forms a *benzoyl* derivative melting at 95°. The *methiodide*,

$C_{10}H_{20}NMe_2I$, crystallises in leaflets melting at 202—203°; the oily nitrosoamine boils at 150—155° under diminished pressure.

*cyclo*Hexanone*iso*oxime, on reduction, yields hexamethyleneimine (b. p. 140°), the *hydrochloride* and *platinichloride* of which are crystalline and melt respectively at 221—224° and 201—203°.

The crystalline *methiodide*, $C_6H_{12}NMe_2I$, decomposing at 260°, is obtained by the action of methyl iodide at the ordinary temperature; the *platinichloride*, $(C_8H_{18}N)_2PtCl_6$, is also crystalline.

Another base containing oxygen, which is also produced in this reduction, has a composition corresponding with the formula $C_6H_{15}NO$; it boils at 238—241° and solidifies in leafy crystals melting at 55—56°; the hydrochloride is very deliquescent, but the *platinichloride*,

$$(C_6H_{15}ON)_2,H_2PtCl_6,$$

has been obtained in a crystalline form.

[With Friedrich Jäger.]—The α-*iso*oxime of β-methyl*cyclo*hexanone yields a secondary cyclic *base*, $C_7H_{15}N$, boiling at 155°; this compound yields a white, hygroscopic hydrochloride, an *aurichloride*,

$$C_7H_{15}N,HAuCl_4,$$

melting at 107°, and a *methiodide*, $C_9H_{20}I$, melting at 210°. A base, $C_7H_{17}NO$, containing oxygen, which is also obtained in this reduction, boils at 245—249°.

The isomeric β-oxime, on reduction, yields a mixture of bases: an *amine* boiling at 130—140°, which furnishes an *aurichloride*, $C_7H_{15}N,HAuCl_4$ or $C_7H_{17}N,HAuCl_4$, melting at 165°; a secondary cyclic *base* boiling at 150—160°, with a *platinichloride* and an *aurichloride* melting respectively at 197° and 111°; an amine, $C_7H_{17}ON$, boiling at 242—245°, which has a composition corresponding with that of an aliphatic compound. The secondary base has a *methiodide*, $C_9H_{20}NI$, melting at 226—227°, from which a crystalline *platinichloride*, $(C_7H_{20}N)_2,PtCl_6$, and a sparingly soluble *aurichloride*, $C_9H_{20}N,AuCl_4$, are obtained.

Menthone*iso*oxime, on reduction, yields a *secondary* cyclic base boiling at 200—205°, which would have the formula

$$\begin{array}{l}CHMe\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CHPr^{\beta}\end{array}\!\!>NH,$$

providing that the original substance has a constitution corresponding with $\begin{array}{l}CHMe-CH_2-CO\\ CH_2\cdot CH_2\cdot CHPr^{\beta}\end{array}\!\!>NH$; on this assumption, the product is 4-*methyl*-7-iso*propylhexamethyleneimine*; it gives rise to a solid *hydrochloride*, $C_{10}H_{21}N,HCl$, a *platinichloride*, $(C_{10}H_{21}N)_2,H_2PtCl_6$, melting at 180°, and a *methiodide*, $C_{12}H_{26}NI$, melting at 236°, which furnishes the *aurichloride*, $C_{12}H_{26}N,AuCl_4$, melting at 114°.

An oxy-base boiling at 140—142° under 10 mm. pressure is also obtained in this reduction; it forms a *benzoyl* derivative melting at 109°. From the results of analysis, it is not possible to decide whether this amine is to be represented by $C_{10}H_{21}ON$ or $C_{10}H_{23}ON$.

The base $C_{20}H_{35}NCl$ (m. p. 59—60°), produced by condensing menthone*iso*oxime with phosphorus pentachloride, when reduced with sodium and amyl alcohol furnishes two basic products, an *amine*, $C_{10}H_{21}N$, which is volatile in steam and yields a crystalline hydro-

chloride, and a bicyclic *base*, $C_{20}H_{40}N_2$ (?), which boils at 203—204° under 16 mm. pressure and forms a sparingly soluble *platinichloride*, $(C_{20}H_{40}N_2),H_2PtCl_6$.

[With VAN BEECK-VOLLENHOVEN.]—The *base* $C_{14}H_{24}ON_2$ results from the action of phosphorus pentachloride on suberone*iso*oxime (α-ketoheptamethyleneimine), crystallises from benzene or light petroleum, and melts at 81—82°; its *aurichloride*, $C_{14}H_{24}ON_2,HAuCl_4$, forms yellow needles melting at 106°; the amine cannot be distilled without decomposing. On reduction with sodium and amyl alcohol, suberone*iso*oxime yields a base containing oxygen, the composition of the substance corresponding approximately with $C_7H_{17}NO$. This amine melts at 48—50°, boils at 250°, and forms a *platinichloride*, $(C_7H_{18}ON)_2PtCl_6$. G. T. M.

Study of Terpenes and Ethereal Oils. Phellandrene. OTTO WALLACH and TH. BÖCKER (*Annalen*, 1902, **324**, 269—280. Compare Abstr., 1902, i, 725).—The lævorotatory diamine obtained by reducing phellandrene nitrite from eucalyptus oil, forms a dextrorotatory *benzoyl* derivative melting at 194—195°, and when treated with methyl iodide in ice cold ethereal solution gives rise to a crystalline *methiodide*, $C_{10}H_{16}N_2Me_6I$ or $C_{10}H_{18}N_2Me_6I$, decomposing at 192°; the corresponding *platinichloride* is insoluble in water. Similar results are obtained with phellandrene nitrite from water-fennel oil; the isomeric lævorotatory diamine also yields a *benzoyl* derivative and methiodide melting respectively at 198—199° and 91—94°. G. T. M.

Chemical Constitution of Copals. MARCEL GUÉDRAS (*Compt. rend.*, 1902, **135**, 797—798).—Madagascar copal gives off gas at 30°, melts at 150°, and distils at 270°. The distillate separates into two layers, an aqueous and an oily. The acid number of the gum is 143, that of the distilled oil is 80. Congo copal begins to melt at 105° and gives a two-layer distillate; the acid number of the gum is 35·55, that of the oil is 24. Kauri copal gives also a two-layer distillate; the acid number of the gum is 69·7, that of the oil is 36.

The oils are soluble in alcohol, ether, benzene, or carbon disulphide. No cinnamic or benzoic acid could be found. When the oil is oxidised with nitric acid, drops are formed which have the odour of camphor. This observation supports the view that the gum contains a partially oxidised terpene. J. McC.

The Resin of Pinus Palustris. ALEXANDER TSCHIRCH and FR. KORITSCHONER (*Arch. Pharm.*, 1902, **240**, 568—574).—*Pinus palustris* is the "long leaf pine" of the United States, and is the chief source of the turpentine and resin prepared there. The resin has an acid number, direct, 81, indirect, 87; a saponification number, 149 cold, 171 hot; an iodine number, 87·9; it is lævorotatory. Retene (8-methyl-5-*iso*propylphenanthrene) and formic, acetic, and succinic acids were identified among the products of its distillation. Water extracts a *bitter substance* from it. From the solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracts amorphous *palabienic acid*, $C_{18}H_{20}O_2$; this melts at 110°, has an acid number 190, corresponding

approximately with monobasicity; a saponification number 236, and an iodine number 66·2, somewhat higher than that corresponding with a monoiodo-derivative; it is apparently not quite pure, but contains a small quantity of a crystalline substance.

From the residual ethereal solution, the 1 per cent. aqueous sodium carbonate extracts a mixture of acids by crystallisation of which from a mixture of methyl and ethyl alcohols, *palabietic acid*, $C_{20}H_{30}O_2$, is obtained; this melts at 153—154°, is optically inactive (when prepared by Mach's method of precipitating the alcoholic solution with gaseous hydrogen chloride, it is lævorotatory), contains neither methoxyl nor hydroxyl groups, has an acid number 182, corresponding with monobasicity, a saponification number 308, and an iodine number 164·8, corresponding with a monoiodo-derivative; the normal *silver* and *lead* salts were prepared, but the only *potassium* salt isolated had the formula $C_{20}H_{29}O_2K,3C_{20}H_{30}O_2$. The alcoholic mother liquor contains amorphous *α*- and *β-palabietinolic acids*, $C_{16}H_{24}O_2$, the lead salts of which are respectively insoluble and soluble in alcohol; both melt at 90—95°, have an acid number 192, corresponding with monobasicity, a saponification number 241 cold, 305 hot, and an iodine number 64·7, corresponding with a monoiodo-derivative.

The residue, obtained by evaporating the ethereal solution now remaining from the preceding extractions, when distilled with steam, yields a dextrorotatory *oil*, which boils at 155—172°, and has the odour of turpentine and a sp. gr. 0·864. After the oil has passed over, *paloresen* remains, unattacked by alkalis.

In 100 parts of the resin there are contained: palabienic acid, 5; palabietic acid, 6—7; palabietinolic acids, 53—57; essential oil, 20—22; paloresen, 10; bitter substance, impurities, and water, 2—3.

From the occurrence of retene among the products of distillation, some conclusions are drawn regarding the structure of abietic acid.

C. F. B.

Russian "White Pitch." ALEXANDER TSCHIRCH and FR. KORITSCHONER (*Arch. Pharm.*, 1902, **240**, 584—596).—"White pitch" (Russian *belji var*) is probably obtained from *Abies Pichta* or from *Picea obovata*; it contains as much as 40 per cent. of woody and other impurities. The resin has an acid number 86, a saponification number in the neighbourhood of 164, and an iodine number 74·6. Water extracts a bitter substance. From the solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracts amorphous *beljiabienic acid*, $C_{13}H_{20}O_2$; this melts at 113—115°, is optically inactive, has an acid number 182, about 2/3 of that corresponding with monobasicity, a saponification number 252, and an iodine number 65·6.

From the ethereal solution, 1 per cent. aqueous sodium carbonate now extracts a mixture of acids, from a solution of which in a mixture of methyl and ethyl alcohols *beljiabietic acid*, $C_{20}H_{30}O_2$, crystallises; this melts at 153—154° when heated slowly, at 160° when heated quickly, is optically inactive, contains no methoxyl groups, has an acid number 182, corresponding with monobasicity, a saponification number 316, corresponding approximately with dibasicity, and an iodine number

163; the *silver* and *lead* salts are normal, if the acid be regarded as monobasic; in the *potassium* salt, only 1/120, instead of 1/30, of the hydrogen is replaced by the metal. The alcoholic mother liquor contains *α*- and *β-beljiabietinolic acids*, $C_{16}H_{24}O_2$, the lead salts of which are respectively insoluble and soluble in alcohol; these acids melt at 88—96°, are optically inactive, have an acid number 210, corresponding approximately with monobasicity, a saponification number 234 cold, 266 hot, and an iodine number 64·8.

When the ethereal solution now remaining is freed from ether and the residue distilled with steam, an *essential oil* comes over; this boils at 158—165°, has sp. gr. 0·863, and is dextrorotatory. *Beljoresen*, $C_{21}H_{36}O$, remains behind; it is indifferent in its behaviour to alkalis.

In 100 parts of the resin there are contained: beljiabienic acid, 4—5; beljiabietic acid, 2·5—3; beljiabietinolic acids, 42—50; essential oil, 20—30; beljoresen, 15—18; bitter substance, colouring-matter, water, and impurities, 1—2. C. F. B.

Herba Gratiolæ. Friedrich Retzlaff (*Arch. Pharm.*, 1902, **240**, 561—568).—The results obtained do not harmonise well with those of Walz (*Jahrb. pr. Pharm.*, **14**, 20; **21**, 1; **24**, 4; *Neues Jahrb. f. Pharm.*, **10**, 65). When the powdered herb *Gratiola officinalis* is mixed into a paste with 50 per cent. alcohol and freshly precipitated lead hydroxide and the paste extracted with 50 per cent. alcohol, a glucoside, *gratiolin*, $C_{43}H_{70}O_{15}$, can be separated from the extract; it is crystalline, has a bitter taste, and melts at 235—237°. When it is heated on the water-bath with alcohol and dilute hydrochloric acid, it yields dextrose and crystalline *gratioligenin*, $C_{37}H_{60}O_{10}$. The latter of these melts at 285° and is tasteless; it is itself a glucoside, and on hydrolysis yields dextrose and *gratiogenin*, $C_{31}H_{50}O_5$, which is crystalline, melts at 198°, and differs from gratioligenin in being soluble in ether. All these substances dissolve in concentrated sulphuric acid, forming a yellow solution which eventually becomes cherry-red with a yellow fluorescence.

Gratiolon is a substance which can be extracted from the herb with ether; it is crystalline and tasteless, and decomposes without melting when heated. It appears to be a polymeride of camphor with the formula $C_{30}H_{48}O_3$; when dissolved in absolute alcohol and treated with sodium, it forms a *sodium* derivative, $C_{30}H_{47}O_3Na$. C. F. B.

Chinese Rhubarb. Alexander Tschirch and K. Heuberger (*Arch. Pharm.*, 1902, **240**, 596—630. Compare Hesse, Abstr., 1900, i, 40; Aweng, Abstr., 1901, i, 39).—The drug was extracted with alcohol, the extract evaporated under diminished pressure, and the residue extracted with different solvents in succession. Ether extracted several hydroxymethylanthraquinones, namely, chrysophanic acid, emodin, and a little rhein (erythroretin is a mixture of these, and so is Dragendorff's and Greenish and Elborne's cathartic acid); also gallic acid and cholesterol. The first was mixed with more or less methyl chrysophanate and melted at 176°; it was not acted on by ammonia (Hesse), neither was it oxidised in alkaline solution by

the oxygen of the air. Rheum-emodin was identified with frangula-emodin by means of its acetyl and benzoyl derivatives. The rhein melted at 313—314° and had the composition $C_{15}H_8O_6$; this formula is that of the methylene ether of a tetrahydroxyanthraquinone, and in fact only a diacetyl derivative, melting at 226—230°, appears to be formed; there is no real evidence of the formation of a tetra-acetyl derivative (Hesse).

The residue left after extraction with ether was then extracted with acetone, the acetone evaporated at a low temperature, and the residue treated with water. The soluble part (Aweng's primary glucoside or double glucoside, Kubly's rheumtannic acid, Hunkel's tannoid) is named *rheotannoglucoside*; when hydrolysed with dilute sulphuric acid, it yielded cinnamic and gallic acids, rheum-red (Kubly's and Hunkel's rheumic acid, Aweng's frangularhamnetin), and a lævorotatory sugar that formed an osazone melting at 205—206° which could be fermented with yeast. Rheotannoglucoside easily becomes converted into a form insoluble in water (Schlossberger and Döpping's aporetin and phaeoretin); this can be reconverted into the soluble form by dissolving it in ammonia and precipitating with acetic acid; if kept for some time, however, it becomes insoluble in alkalis. The part of the acetone extract insoluble in water (Aweng's secondary glucoside, frangulic acid) consisted of this insoluble form of the rheotannoglucoside mixed with a little *rheoanthraglucoside* (Gilson's chrysophan); when hydrolysed, it yielded chrysophanic acid, emodin, rheum-red, rheonigrin, a dextrorotatory sugar which forms an osazone melting at 205° and does not undergo fermentation, and a little cinnamic and gallic acids.

The residue from these extractions did not yield any other definite products, either in the aqueous and benzene-alcoholic extracts or in the portions insoluble in these solvents.

The residue left after the original extraction of the drug with alcohol yielded proteid substances and a little rheonigrin when extracted with 5 per cent. aqueous ammonia. By extracting another portion of the drug successively with ether and 20 per cent. ammonia, and precipitating the second extract with hydrochloric acid, anthraglucorhein and rheonigrin were obtained; the former is soluble and the latter insoluble in alcohol. The former yielded chrysophanic acid, emodin, rhein, and rheum-red when boiled in alcoholic solution with hydrochloric acid; a mixture of the last three was converted almost entirely into rheonigrin after it had been kept for a year. Rheonigrin is thus connected with the hydroxymethylanthraquinones, and is possibly a product of polymerisation; moreover, it yields chrysamic acid,

$$C_{14}H_2O_2(NO_2)_2(OH)_2$$

(Garot's erythrose), when it is boiled with concentrated nitric acid.

No rhabarberone (Hesse) was detected.

The purgative action of rhubarb is due to the rheoanthraglucoside; and to some extent to the free hydroxymethylanthraquinones, as has been shown in the case of chrysophanic acid and emodin. The rheotannoglucoside has no aperient action; on the contrary, it is tonic and mildly astringent. C. F. B.

[Theory of] Dyeing. A. BINZ and GEORG SCHROETER (*Ber.*, 1902, **35**, 4225—4229).—The so-called "salt" theory of dyeing, which assumes that a salt is produced between the acid or basic dyes and the amino-acids of the wool or silk, is shown in several cases to be untenable, since certain acid colouring matters will dye in the presence of an excess of sodium hydroxide, and some basic dyes in the presence of strong hydrochloric acid. Dyeing experiments are described with the following: azobenzenesulphonic acids, *p*-hydroxyazobenzene, *p*-aminoazobenzene, *p*-dimethylaminoazobenzene, *m* : *m'*-diaminoazobenzene, and tetramethyl-*m* : *m'*-diaminoazobenzene. R. H. P.

Red Pigments of Alkanna Root. H. GAWALOWSKI (*Chem. Centr.*, 1902, ii, 1001; from *Zeit. Oesterr. Apoth.-V.*, **40**, 1001—1002).—Alkanna root contains two red pigments named alkannic acid and anchusic acid respectively. *Anchusic acid* (probably $C_{30}H_{39}O_7$), obtained by extracting the root with benzene, forms a brownish-red mass, is soluble in light petroleum, and gives a green coloration with alkalis and a violet-green with ammonia. *Alkannic acid* (probably $C_{30}H_{28}O_8$) may be obtained from the root after removal of the other pigment by treatment with alcohol or ether or a mixture of the two; the extract, on evaporation, leaves a residue which contains some resin. Alkannic acid, a brownish-red mass, is soluble in alcohol, ether, benzene, or light petroleum, and, with alkalis, gives an indigo-blue coloration, with ammonia, an ultra-violet blue shade. Both acids form metallic salts of characteristic colour, and the alkali salts seem to be very suitable for use as indicators. Alkannic acid, in presence of alcohol, changes into anchusic acid; the change takes place more readily in the presence of the resin mentioned above and is also aided by light. E. W. W.

Conversion of Atropine into *d*- and *l*-Hyoscyamines. T. AMENOMIYA (*Arch. Pharm.*, 1902, **240**, 498—504).—Since it has been discovered (Gadamer, Abstr., 1901, i, 605) that the tropine residue in both hyoscyamine and atropine is inactive, it can hardly be doubted that the substances described as *d*- and *l*-atropines (Ladenburg and Hundt, Abstr., 1890, 75) were in reality mixtures of atropine with the *d*- and *l*-hyoscyamines. The preparation of these substances was therefore repeated. Atropine was decomposed into tropic acid and tropine by prolonged boiling of its solution in water containing a little alcohol; the tropic acid was separated into its optical isomerides by crystallisation of its quinine salt, and finally each isomeride was mixed with tropine in 5 per cent. alcoholic hydrochloric acid, the condensation being effected by evaporating the solution to a small bulk. The product was purified by means of its crystalline aurichloride; the latter was converted into the hydrochloride by the action of hydrogen sulphide, and from this salt the alkaloid was liberated with ammonia. A comparison of the physical properties leaves little doubt that the substances thus synthesised were the optically isomeric hyoscyamines:

	M. p. of the aurichloride.	$[\alpha]_D$ of the hydrochloride.	M. p. of the alkaloid.
l-Hyoscyamine, natural.........	158—159°	−25·07°	108°
l-Hyoscyamine, synthetical ...	158—159	−23·15	103
r-Hyoscyamine, synthetical ...	158—159	+24·12	106

C. F. B.

Ephedrine. EMERSON R. MILLER (*Arch. Pharm.*, 1902, **240**, 481—498. Compare Nagai, *Berl. klin. Wochschr.*, 1887, No. 38; *Chem. Zeit.*, 1900, **1**, 441; Merck, *Merck's Bericht.*, 1893, 13; Takahashi and Miura, *Jahrb. Pharm.*, 1900).—From a specimen of *Ephedra vulgaris var. helvetica*, only ψ-ephedrine (Ladenburg and Oelschlägel, Abstr., 1889, 1020) could be isolated; no appreciable amount of ephedrine was found.

Ephedrine is a monoacid base, to which the formula

$$CH_2Ph\cdot CH(NHMe)\cdot CH_2\cdot OH$$

has been assigned. The starting point in the present investigation was the hydrochloride obtained from Merck. It melted at 216° and had $[\alpha]_D$ −36·66° in 5 per cent. aqueous solution at 15°. The platinichloride melted at 186°, the base itself at 40°. The iodide, aurichloride, and platinichloride of quaternary methylephedrinemethylammonium melt at 203°, 188—190°, and 247° respectively.

Ephedrine will not react with either hydroxylamine, phenylhydrazine, or acetyl chloride. With benzoyl chloride, it yields a *dibenzoyl* derivative, $C_{10}H_{13}ONBz_2$, melting at 115—116°. With acetic anhydride and sodium acetate, the hydrochloride forms a *monoacetyl* derivative, the *platinichloride* of which, $2C_{10}H_{14}ONAc,H_2PtCl_6$, melts at 210°; in the absence of sodium acetate, a *platinichloride* was obtained with the same composition, but melting at 185°; possibly in one the acetyl group was attached to nitrogen, in the other to oxygen. Methylephedrinemethylammonium iodide, when heated with the equivalent quantity of silver acetate and an excess of acetic anhydride, forms a *monoacetyl* derivative, the *platinichloride* of which,

$$(C_{10}H_{13}ONMeAc)_2Me_2PtCl_6,$$

melts at 186—188°; in this, the acetyl group must be attached to oxygen. When ephedrine is treated with methyl iodide in methyl alcoholic solution, ephedrinemethylammonium iodide is formed along with the quaternary iodide, which is the main product of the reaction; its *platinichloride*, $2C_{10}H_{14}ONMe,H_2PtCl_6$, melts at 155—160°, the corresponding *aurichloride* at 121—123°. When a dilute aqueous solution of methylephedrinemethylammonium hydroxide is distilled, an *oil* comes over which boils at 205—210° and has the composition $C_9H_{10}O$; probably it is an aromatic alcohol with unsaturated side chain. The basic products were isolated in the form of platinichlorides and consisted of trimethylamine and a *base*, the *platinichloride* of which, $(C_{10}H_{14}ONMe)_2,Me_2PtCl_6$, melts at 226° and combines with trimethylammonium platinichloride in molecular proportions to form a *compound*, melting at 210—211°. C. F. B.

Musculamine, a Base derived from Muscles. ALEXANDRE ÉTARD and A. VILA (*Compt. rend.*, 1902, **135**, 698—700).—After separating

from the products of hydrolysis of calf-muscle tyrosine, glycine, leucine, and glutamic acid, there remains a very complex syrup, which is soluble in methyl alcohol. Phosphotungstic acid produces an abundant precipitate with this solution. To effect a separation of the various basic substances present, benzoylation was tried; the reaction being carried out by the Schotten-Baumann method, only barium hydroxide was used instead of sodium hydroxide. The curdy mass obtained by this process was filtered from the alkaline solution and dissolved in boiling water. The *benzoyl* derivative, $C_8H_{18}N_3Bz_3$, crystallises in slender needles and boils without decomposition at (about) 360°. [The melting point is not given.] By hydrolysis with sodium hydroxide, a liquid *base* is obtained; the *hydrochloride*, $C_8H_{21}N_3,3HCl$, is crystalline, and yields an orange platinichloride. This new base, for which the name *musculamine* is suggested, does not resemble arginine, and does not appear to belong to the guanidine group. K. J. P. O.

Musculamine, the Base derived from Muscles. SWIGEL POSTERNAK (*Compt. rend.*, 1902, **135**, 865—866).—Étard and Vila have recently (preceding abstract) described a base, *musculamine*, $C_8H_{21}N_3$, which is obtained in the hydrolysis of muscles. It is shown that the analytical numbers agree equally well with those required by the base cadaverine (pentamethylenediamine), $C_5H_{10}\cdot(NH_2)_2$, which, up to the present, has not been obtained in the hydrolysis of proteids.
K. J. P. O.

Normal Quinine Hydrobromide. OSWALD HESSE (*Chem. Centr.*, 1902, ii, 953; from *Süddeut. Apoth.-Zeit.*, **42**, 621—622).—Quinine hydrobromide, $C_{20}H_{24}O_2N_2,HBr,H_2O$, is somewhat hygroscopic, dissolves in about 55 parts of water at 15° or in 1 part of boiling water, and is readily soluble in alcohol or chloroform, but only very sparingly so in ether. The salt may be dried at 50—55°, but does not lose its water of crystallisation below 100°. E. W. W.

Compounds of Bismuth Salts with Organic Bases. II. CLEMENTE MONTEMARTINI (*Gazzetta*, 1902, **32**, ii, 178—181. Compare Abstr., 1901, i, 163).—Further investigation shows that the compound of bismuth chloride with pyridine obtained by the author on adding this base to an ethereal solution of the bismuth chloride (*loc. cit.*) is not identical with that described by Vànino and Hauser (Abstr., 1901, i, 289), who worked with an acetone solution of the salt, whilst neither of these compounds possesses the composition $(C_5H_5N)_3(BiCl_3)_2$, previously assigned to them.

With bismuth chloride or bromide, quinoline yields different products according as the reaction is carried out in ethereal or in acetone solution. T. H. P.

Some Pyridine Compounds of Metallic Salts of Organic Acids. FRITZ REITZENSTEIN (*Zeit. anorg. Chem.*, 1902, **32**, 298—318. Compare Abstr., 1899, i, 160).—The author has extended his observa-

tions on the pyridine compounds of organic salts of bivalent metals in order to compare these with the ammonia derivatives and the hydrates. Theoretical considerations are postponed until more data are obtained. Unless otherwise stated, the compounds are formed by heating the salts with pyridine.

Cobaltous acetate dipyridine, $Co(C_2H_3O_2)_2,2C_5H_5N$, is a chocolate-coloured substance which becomes reddish at 100° and melts to a dark blue liquid at 112—114°. It is soluble in alcohol or chloroform to a red solution.

Cobaltous monochloroacetate tetrapyridine, $Co(CH_2Cl{\cdot}CO_2)_2,4C_5H_5N$, forms red crystals which, on drying between filter-paper, become dark blue. In the desiccator in a pyridine atmosphere, the salt again becomes red. When exposed to the air for some weeks, it becomes blue and is transformed into $Co(CH_2Cl{\cdot}CO_2)_2,2{\cdot}5C_5H_5N,1{\cdot}5H_2O$.

Cobaltous dichloroacetate pentapyridine, $Co(CHCl_2{\cdot}CO_2)_2,5C_5H_5N$, forms red crystals which melt at 151° to a bluish-violet liquid.

Cobaltous trichloroacetate tetrahydrate, $Co(CCl_3{\cdot}CO_2)_2,4H_2O$, obtained from trichloroacetic acid and cobalt carbonate, is a red, crystalline substance with the odour of fresh fruit. It is soluble in ether.

Cobaltous trichloroacetate tetrapyridine, $Co(CCl_3{\cdot}CO_2)_2,4C_5H_5N$, formed by shaking an ethereal solution of cobalt trichloroacetate with pyridine, is a crimson compound very sparingly soluble in cold water. When heated at 100°, it gives a grey-green powder of the tripyridine compound, and in a pyridine atmosphere it absorbs more of the base to form a hexapyridine derivative.

Cobaltous thiocyanate tetrapyridine, $Co(CNS)_2,4C_5H_5N$, is obtained by dissolving hydrated cobaltous chloride in alcohol and shaking with potassium thiocyanate and pyridine. It is obtained as a peach-coloured precipitate which is soluble, with a yellow colour, in ammonia, and gives an ultramarine blue colour when treated with dilute sulphuric acid or hydrochloric acid. It can be crystallised from alcohol.

Nickelous acetate dipyridine, $Ni(C_2H_3O_2)_2,2C_5H_5N$, is obtained in blue crystals, which melt at 145—147° to a green liquid.

Nickelous monochloroacetate hexapyridine, $Ni(CH_2Cl{\cdot}CO_2)_2,6C_5H_5N$, forms bluish-green crystals which quickly lose pyridine and produce a bluish-green tetrapyridine derivative. When warmed with absolute alcohol, a yellowish substance is formed, which is a monopyridine compound.

Nickelous trichloroacetate tetrapyridine, $Ni(CCl_3{\cdot}CO_2)_2,4C_5H_5N$, is a light blue substance which absorbs pyridine, giving a green hexapyridine compound. When heated at 100°, the residue consists of the monopyridine derivative.

The nickel salts were obtained by the methods employed in forming the corresponding cobalt salts.

Ferrous lactate dipyridine, $Fe(C_3H_5O_3)_2,2C_5H_5N$, is formed by heating hydrated ferrous lactate with pyridine and precipitating with ether. It is a yellow substance which completely loses pyridine at 100°.

Anhydrous ferrous lactate does not combine with pyridine.

When hydrated zinc acetate is boiled with pyridine, a tetrapyridine compound appears to be formed which easily loses pyridine and gives

the monopyridine derivative. From anhydrous zinc acetate and pyridine, a *zinc acetate dipyridine*, $Zn(C_2H_3O_2)_2,2C_5H_5N$, has been isolated.

Zinc lactate dipyridine, $Zn(C_3H_5O_3)_2,2C_5H_5N$, separates from the solution of zinc lactate in pyridine.

Cadmium acetate tripyridine, $Cd(C_2H_3O_2)_2,3C_5H_5N$, is formed by boiling either hydrated or anhydrous cadmium acetate with pyridine. When heated at 100°, it loses pyridine.

Cadmium monochloroacetate tripyridine, $Cd(CH_2Cl\cdot CO_2)_2,3C_5H_5N$, is obtained from the syrup made by mixing precipitated cadmium hydroxide with monochloroacetic acid by adding pyridine. Large, white crystals separate which can be recrystallised from 50 per cent. alcohol.

Cadmium trichloroacetate and pyridine do not give a homogeneous product.

The product obtained by the action of pyridine on mercuric monochloroacetate depends on the temperature.

Mercuric monochloroacetate dipyridine, $Hg(CH_2Cl\cdot CO_2)_2,2C_5H_5N$, has been isolated: it melts at 110°. In another preparation, in which the temperature was higher, a product was obtained which may be a mixture of a normal pyridine derivative with a basic pyridine-betaine hydrochloride. J. McC.

Condensation Products from α-Pyridyl Methyl Ketone with Benzaldehyde and *o*-Nitrobenzaldehyde. Carl Engler and Adalbert Engler (*Ber.*, 1902, **35**, 4061—4066).—In order to investigate the influence of the nitro-group on the formation of aldols, the following substances have been prepared. *α-Pyridyl methyl ketone* only condenses with benzaldehyde in the presence of sodium hydroxide with the simultaneous elimination of water and formation of *α-pyridyl styryl ketone*, $C_5NH_4\cdot CO\cdot CH{:}CHPh$; it crystallises in greenish-yellow leaflets melting at 75°; the *platinichloride* is a yellow, crystalline precipitate; the *hydrochloride* is yellowish-green and melts at 150—153°; the *mercurichloride* is yellow powder, which becomes coloured at 140° and melts at 173°. *Benzylidenedimethyl-α-pyridyl ketone*, $CHPh(CH_2\cdot CO\cdot C_5NH_4)_2$, prepared from benzaldehyde and the ketone, crystallises in needles melting at 152°; it forms a *platinichloride* melting at 206°, and a *mercurichloride* melting at 122°.

Dibenzylidenetrimethyl-α-pyridyl ketone,

$$C_5NH_4\cdot CO\cdot CH(CHPh\cdot CH_2\cdot CO\cdot C_5NH_4)_2,$$

is also formed from benzaldehyde and α-pyridyl methyl ketone, and forms crystals melting at 215°.

*α-Pyridyl-*o*-nitrophenyllactyl ketone*,

$$C_5NH_4\cdot CO\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot NO_2,$$

prepared by the action of sodium hydroxide on a mixture of α-pyridyl methyl ketone and *o*-nitrobenzaldehyde, forms white crystals melting at 106°; the *mercurichloride* melts at 164°; the *chromate* melts and decomposes at 141°; the *platinichloride* is a yellow precipitate melting and decomposing at 179°. Addition of a few drops of concentrated sodium hydroxide to an alcoholic solution of the aldol leads to the

immediate formation of indigotin. cis-*a-Pyridyl-o-nitrostyryl ketone*, $C_5NH_4 \cdot CO \cdot CH:CH \cdot C_6H_4 \cdot NO_2$, is obtained when a certain concentration of alcohol has been used in condensing *a*-pyridyl methyl ketone and *o*-nitrobenzaldehyde; it crystallises in green leaflets melting at 153°; the *platinichloride* is a pale yellow precipitate decomposing at 180°. trans-*a-Pyridyl-o-nitrostyryl ketone* is obtained by using concentrated solutions in pure alcohol; it forms crystalline aggregates melting at 141°, and on boiling with sodium hydroxide is converted into indigotin. The *platinichloride* forms a dark yellow, crystalline precipitate decomposing at 174°; the *aurichloride* is a dark yellow precipitate; the *phenylhydrazone* forms yellow crystals melting at 137°; the *tetrabromide* forms greenish needles, which become dark at 112° and melt at 120°; the *picrate* decomposes at 152°, the *hydrochloride* melts at 163°. K. J. P. O.

Action of Alkyl Iodides on the Indoles. GIUSEPPE PLANCHER (*Atti Real. Accad. Lincei*, 1902, [v], **11**, ii, 182—187. Compare Abstr., 1900, i, 560).—The author has previously found (*loc. cit.*) that in the action of methyl iodide on 3-methyl-2-*iso*propylindole the *iso*propyl group changes its position, the product obtained being 1 : 2 : 3-trimethyl-3-*iso*propylindoline, and not the 1 : 3 : 3-trimethyl-2-*iso*propylindoline, which was expected. This result is now confirmed by the observation that the hydriodide of the last-named compound, when maintained at a temperature of 180—190° for a few minutes, is converted into 1 : 2 : 3-trimethyl-3-*iso*propylindoline hydriodide. The same compound is obtained by the action of *iso*propyl iodide on 1 : 2 : 3-trimethylindole. By regulating the temperature at which the interaction of methyl iodide and 3-methyl-2-*iso*propylindole takes place, the intermediate product, 2 : 3-dimethyl-3-*iso*propylindolenine, may be obtained. This action thus proceeds in either of two directions: 3-methyl-2-*iso*propylindole and methyl iodide yielding either 3 : 3-dimethyl-2-*iso*propylindolenine and 1 : 3 : 3-trimethyl-2-*iso*propylideneindoline; or 2 : 3-dimethyl-3-*iso*propylindolenine and 1 : 3-dimethyl-3-*iso*propyl-2-methyleneindoline.

These results show that the heavy radicle possesses a great tendency to pass from the 2- to the 3-position, but such a migration is not necessary in order that the indoles may be converted into indolines, as is shown by the action of methyl iodide on 1 : 3-dimethyl-2-ethylindole.

1 : 3-*Dimethyl-2-ethylindole*, $C_{12}H_{15}N$, prepared by condensing the phenylmethylhydrazone of diethylketone by heating with zinc chloride, boils under the ordinary pressure at 285—287° and has a faint fœcal odour; its *picrate* crystallises from benzene in dark chestnut-coloured plates melting at 91°. The action of methyl iodide on 1 : 3-dimethyl-2-ethylindole yields 1 : 3 : 3-trimethyl-2-ethylideneindoline, no transposition of the heavier ethyl radicle taking place in this case.

[With L. FORGHIERI.]—2-tert.*Butylindole*, $C_{12}H_{15}N$, prepared from pinacolinephenylhydrazone by condensing it in presence of zinc chloride, distils undecomposed at 276—279° at the ordinary pressure and crystallises from light petroleum in colourless, almost odourless scales

melting at 73°; its *picrate* is reddish-brown and melts at 133°. On treatment with amyl nitrite in presence of sodium ethoxide, the butylindole yields the sodium derivative of the corresponding nitrosobutylindole; the latter, obtained by treating the sodium salt suspended in water with carbon dioxide, separates from ether in yellow crystals melting at 233°, thus showing that the butyl group is still in the 2-position.

When heated in a closed tube with methyl iodide, 2-*tert.*butylindole yields 1 : 3 : 3-trimethyl-2-methyleneindoline hydriodide, β-methylpropylene, and hydrogen iodide. In this case, the *tert.*butyl iodide, although eliminated from the molecule, does not alkylate the indole in the 3-position, since it is decomposed at the temperature of the reaction into β-methylpropylene and hydrogen iodide. T. H. P.

Synthesis of a Pyrhydrindene Derivative from a Semicyclic 1 : 5-Diketone of the Pentamethylene Series. HANS STOBBE and HANS VOLLAND (*Ber.*, 1902, 35, 3973—3977. Compare Abstr., 1902, i, 472).—6-Phenacyl-5-benzyl*cyclo*pentanone (*loc. cit.*) is more easily prepared from *cyclo*pentanone and benzylideneacetophenone by employing a secondary base as condensing agent instead of sodium hydroxide. With hydroxylamine, this diketone only gives a *monoxime*, which crystallises in long needles melting at 154—155°. When the diketone is heated in alcoholic solution with hydroxylamine hydrochloride under pressure at 120—130° for 4 hours, or when a solution of the oxime in benzene is saturated with hydrogen chloride, 5 : 7-*diphenylpyrhydrindene*, $\begin{matrix} CH\cdot CPh\colon C\cdot CH_2 \\ CPh—N\colon C\cdot CH_2 \end{matrix} > CH_2$, is obtained; the base crystallises in long, colourless prisms melting at 145—146°; the *hydrochloride* prepared by passing hydrogen chloride into an ethereal solution of the base is crystalline and melts at 225°; the *picrate* crystallises in golden-yellow needles melting at 208—209°; the *methiodide* forms yellowish-green needles which melt and decompose at 240—241°. K. J. P. O.

***Bz*-Tetrahydroquinoline Derivatives from Semicyclic 1 : 5-Diketones of the *cyclo*-Hexane Series.** HANS STOBBE [and, in part, MAX HELLER] (*Ber.*, 1902, 35, 3978—3981. Compare preceding abstract).—When the 1 : 5-diketone, 6-phenacyl-6-benzyl-3-methyl*cyclo*hexanone, previously described (Abstr., 1902, i, 472), is boiled in anhydrous solution with hydroxylamine hydrochloride, or when the oxime of the diketone is treated in benzene solution with dry hydrogen chloride, water is eliminated and a base, 2 : 4-*diphenyl*-7-(or 5-)-*methyl*-Bz-*tetrahydroquinoline*, $\begin{matrix} CH\cdot CPh\colon C\cdot CH_2\cdot CH_2 \\ CPh—N\colon C\cdot CH_2\cdot CHMe \end{matrix}$ or

$$\begin{matrix} CH\cdot CPh\colon C\cdot CHMe\cdot CH_2 \\ CPh—N\colon C—CH_2—CH_2 \end{matrix},$$

is formed; it crystallises in short, pale yellow prisms or plates melting at 112—113°, and dissolves in sulphuric acid with a yellow colour and an intense bluish-violet fluorescence; the *hydrochloride* formed by passing hydrogen chloride into an ethereal solution consists of white flakes;

the *platinichloride* is orange-coloured; the *picrate* forms yellow needles decomposing at 192—200°. This substance is a tertiary base and forms a *methiodide*, $C_{22}H_{21}N,MeI$, which melts at 204—206°. On oxidation with permanganate, instead of obtaining a diphenylpyridinedicarboxylic acid or a pyridinetetracarboxylic acid, the main product was benzoic acid.

The author uses the prefix *Bz* to denote the fact that the benzene ring is hydrogenised, and not the pyridine ring. K. J. P. O.

Ethylallyltetrahydroquinolinium Iodide. EDGAR WEDEKIND and R. OECHSLEN (*Ber.*, 1902, **35**, 3907—3910).—*Ethylallyltetrahydroquinolinium iodide*, $\begin{matrix}CH_2\text{--}CH_2\\ | \\ CH_2\cdot C_6H_4\end{matrix}\!\!>\!NEtI\cdot C_3H_5$, from ethyltetrahydroquinoline and allyl iodide, crystallises in pale yellowish flakes and decomposes at 119—120°; the *platinichloride*, $(C_{14}H_{19}N)_2,H_2PtCl_6$, separates from hot water in yellow crystals and decomposes at 158—159°.

Ethyl iodide and allyltetrahydroquinoline, on the other hand, yield ethylene and *allyltetrahydroquinoline hydriodide*, which separates from a mixture of acetone and ether in yellowish-white, microscopic crystals and melts at 169—170°. T. M. L.

***iso*Quinoline and Quinoline Betaines.** HILDRICH IHLDER (*Arch. Pharm.*, 1902, **240**, 504—520. Compare Vongerichten, Abstr., 1882, 1254; Rhoussopoulos, Abstr., 1883, 96).—*iso*Quinoline condenses with ethyl bromoacetate in ethereal solution to form *ethyl* iso*quinolineacetate hydrobromide*, $C_9NH_7Br\cdot CH_2\cdot CO_2Et$, which melts at 199°. When this is digested with silver chloride and water in the cold, it is converted into the corresponding *hydrochloride*, which melts at 183—186°; the *aurichloride* and *platinichloride* melt at 122° and 201—205° respectively. If the digestion is effected on the water-bath, alcohol is eliminated and iso*quinolinebetaine chloride*, $C_9NH_7{<}^{CH_2}_{O}{>}CO,HCl$, is formed, melting at 204°; this forms an abnormal *aurichloride*, $3C_9NH_7{<}^{CH_2}_{O}{>}CO,2HAuCl_4,2H_2O$, melting at 127°, along with the more soluble normal salt, which melts at 118°; it forms also a corresponding abnormal *platinichloride* melting at 199—207°.

*iso*Quinoline and chloroacetic acid form a *compound*

$$C_9NH_7Cl\cdot CH_2\cdot CO_2H,2C_9NH_7{<}^{CH_2}_{O}{>}CO,HCl,2H_2O\,;$$

when this is dried or crystallised, it yields the betaine chloride mentioned above, from which the normal platinichloride, melting at 221—224°, was obtained. At the same time, another and less soluble *compound*, $OH\cdot C_9NH_7\cdot CH_2\cdot CO_2H,C_9NH_7{<}^{CH_2}_{O}{>}CO,HCl$, melting at 157°, is formed; this yields the betaine chloride when it is boiled with hydrochloric acid, and can be converted into the abnormal aurichloride.

Quinoline condenses with ethyl bromoacetate in ethereal solution to

ethyl quinolineacetate hydrobromide, $C_9NH_7Br\cdot CH_2\cdot CO_2Et$, which melts at 180°. When it is dissolved in alcohol and precipitated by covering the solution with a layer of ether, it is converted in part into the *compound* $2C_9NH_7{<}{\substack{CH_2\\O}}{>}CO,HBr$, which melts at 200°. From quinolinebetaine chloride, only the normal aurichloride could be obtained

The chlorine indicated in the above formulæ as HCl could be titrated with aqueous sodium hydroxide; but not that contained in C_9NH_7Cl, the latter, however, could be precipitated with silver nitrate. The abnormal aurichlorides mentioned separated out when but little hydrochloric acid was present in the liquid; but as a rule the normal salt was formed in the presence of much acid. C. F. B.

Cinchomeronic and Apophyllenic Acids. KARL KAAS (*Monatsh.*, 1902, **23**, 681—687).—The dimethyl ester of cinchomeronic acid is converted by cautious hydrolysis into a *β-acid ester* isomeric with the known γ-ester. It melts at 160° and forms a light blue copper salt; the *methiodide* melts at 188°, and when heated above its melting point is converted into methyl nicotinate, and cinchomeronic and apophyllenic acids. E. F. A.

Esters of Cinchomeronic Acid, and Apophyllenic Acid. ALFRED KIRPAL (*Monatsh.*, 1902, **23**, 765—772. Compare Abstr., 1900, i, 51, and preceding abstract).—The author describes the compounds formed from cinchomeronic acid and methyl iodide. If the anhydride is heated with the iodide and the methiodide shaken with silver oxide and water, apophyllenic acid is obtained; but on using methyl alcohol in place of water, *cinchomeronic methylbetaine methyl ester* is formed, which crystallises in long, colourless prisms melting at 218°. By the action of thionyl chloride, apophyllenic acid is converted into the methochloride of cinchomeronic anhydride.

E. F. A.

Naphthastyril. GEORG SCHROETER and HUBERT RÖSSLER (*Ber.*, 1902, **35**, 4218—4224).—*Ethyl* 1 : 8-*naphthastyrilacetate*, obtained when the sodium derivative of naphthastyril is treated with ethyl chloroacetate, crystallises in clusters of yellow needles melting at 86—87° and, when treated with an alcoholic solution of sodium ethoxide, yields first the yellow, crystalline *sodium* salt of the corresponding acid and then the white, crystalline *disodium* salt of 1 : 8-naphthylglycinecarboxylic acid. Both salts, when treated with acids, yield *naphthastyrilacetic acid*, $C_{10}H_6{<}{\substack{CO\\ | \\N\cdot CH_2\cdot CO_2H}}$, which separates from glacial acetic acid in sulphur-yellow crystals melting at 258—259°. 1 : 8-Naphthylglycinecarboxylic acid does not exist, its silver salt is very unstable, and does not yield an ester when treated with methyl iodide.

Ethyl 1 : 8-*naphthastyrilphenylacetate*, $C_{10}H_6{<}{\substack{CO\\ | \\N\cdot CHPh\cdot CO_2Et}}$, from ethyl phenylbromoacetate and the sodium derivative of naphthastyril,

crystallises from H_2O and melts at 105—106°. The *acid* crystallises from alcohol in small, yellow needles and melts at 186—187°. The ester, when boiled with an alcoholic solution of sodium methoxide, yields the *disodium* salt of 1 : 8-carboxynaphthylaminophenylacetic acid.

Tetrahydro-1 : 8-*aminonaphthoic acid*, obtained when naphthastyril is reduced with sodium amalgam, crystallises from alcohol in grey laminæ which melt and decompose at 160—161°. The silver salt forms the additive compound, $2NH_2{\cdot}C_{10}H_{10}{\cdot}CO_2Ag,AgNO_3$. The *methyl* ester crystallises from light petroleum and melts at 53—54° and its *hydrochloride* crystallises in long needles. *Acetyltetrahydronaphthastyril* crystallises in needles melting at 103—104° and the *acetyl* derivative of the above acid melts at 181—182°. The acid, when diazotised and coupled with β-naphthol, yields a red dye.

R. H. P.

Naphthacridinedisulphonic Acids. RICHARD MÖHLAU and O. HAASE (*Ber.*, 1902, **35**, 4172—4177).—α-Naphthylamine does not yield well-defined products with formaldehyde (compare Senier and Goodwin, Trans., 1902, **81**, 288).

β-*Naphthacridine*-3 : 10-*disulphonic acid*, $C_{21}H_{11}N(SO_3H)_2$, is readily obtained when aqueous formaldehyde is slowly dropped into a boiling solution of 2 : 6-naphthylaminesulphonic acid ; it is very sparingly soluble in hot water, readily so in ammonia and alkalis. The *silver* salt is a gelatinous precipitate.

α-*Naphthacridine*-2 : 12-*disulphonic acid* crystallises in golden-yellow plates soluble in warm water, yielding solutions which exhibit a pale bluish-violet fluorescence. It is obtained when sodium naphthionate, formaldehyde solution, and water are heated in an autoclave under 10 atmospheres pressure and the resulting product—probably a mixture of the sodium salts of the disulphonic acid and of its hydro-derivative—oxidised with permanganate. The *sodium* salt crystallises from water in colourless needles.

Solutions of the disulphonic acids, when warmed, lose their colour to a large extent, but this returns as the solution cools or on the addition of a little mineral acid. It is suggested that each acid occurs in two distinct forms, a colourless variety, with the normal constitution, and a coloured isomeride, in which internal salt formation has occurred between one of the sulphonic acid groups and the nitrogen atom.

J. J. S.

Action of Methyl Sulphate on Michler's Ketone and on Auramine. OTTO ZOHLEN (*J. pr. Chem.*, 1902, [ii], **66**, 387—400).—The action of methyl sulphate on Michler's ketone leads to the formation of *hexamethyldiaminobenzophenone dimethosulphate*,

$$CO(C_6H_4{\cdot}NMe_3{\cdot}SO_4Me)_2,$$

which crystallises in white leaflets, melts at 186—187°, has a bitter taste, is easily soluble in water, glacial acetic acid, or aqueous alcohol, but sparingly so in absolute alcohol or acetone, evolves formaldehyde when heated with oxidising agents, and, on fusion with alkalis or on exposure to air, regenerates Michler's ketone with evolution of methylamines. The following salts of hexamethyldiaminobenzophenone are

described: the *platinichloride*, $C_{19}H_{26}ON_2PtCl_6$, forms small, yellow leaflets and decomposes at about 220°; the *trichromate*,

$$C_{19}H_{26}ON_2,Cr_3O_{10},2H_2O,$$

forms light brown crystals and melts and decomposes at 200—210°; the *picrate* crystallises in yellow grains and melts at 222—223°; the *hydrobromide*, $C_{19}H_{26}ON_2Br_2,2H_2O$, crystallises in yellow prisms and melts and decomposes at 168°; the *hydriodide*, $C_{19}H_{26}ON_2I_2,3H_2O$, crystallises in yellow plates and melts at 171—172°. The *dihydroxide*, prepared from the hydriodide, forms small, white crystals, is easily soluble in water, glacial acetic acid, or alcohol, colours litmus green in aqueous solution, and reddens aqueous phenolphthalein solution when hot, but not in the cold. The base has a very bitter taste, and tends to decompose with evolution of the methylamines.

The action of methyl sulphate on auramine leads to the formation of *methylauramine methosulphate*,

$$NHMe\cdot C(C_6H_4\cdot NMe_2)\colon C_6H_4\colon NMe_2\cdot SO_4Me,$$

and hexamethyldiaminobenzophenone dimethosulphate, the latter being formed by hydrolysis of the methylauramine, which takes place slowly in cold, more rapidly in boiling, water. Methylauramine methosulphate forms golden-yellow flakes, melts at 225°, has a bitter taste, and is easily soluble in water, alcohol, or glacial acetic acid, more sparingly so in acetone, and insoluble in ether. The methosulphate evolves formaldehyde when heated with oxidising agents, forms barium sulphate with barium chloride only on prolonged boiling with concentrated hydrochloric acid, and on addition of ammonia yields *methylauramine*, which forms yellow flakes, crystallises in thick crystals having a greenish tinge, melts at 133°, and is easily soluble in alcohol or glacial acetic acid. *Methylauramine platinichloride* forms reddish-yellow leaflets, decomposing at 190—200°; the *picrate*, glistening, reddish-yellow leaflets, decomposing at 225°; the *trichromate*, long, reddish-brown leaflets, decomposing at 70°; the *thiocyanate*, long, yellow leaflets, melting at 213—214°; the *hydrochloride*, yellow leaflets, melting at 225°; the *hydrobromide*, long needles, melting at 260°, and the *hydriodide*, long needles, melting at 259°.

The absorption spectrum of methylauramine methosulphate in alcoholic solution resembles that of auramine, but the absorption band lies more towards the green.

Methylauramine tri-iodide, $C_{18}H_{24}N_2I,I_2$, crystallises in acicular crystals, melts at 178°, appears reddish-brown by transmitted, pale violet by reflected, light, and is easily soluble in warm alcohol. The *pentaiodide* crystallises in glistening, metallic, rhombic crystals, melts at 128—129°, appears green by reflected light, and is easily soluble in warm alcohol. The *heptaiodide* crystallises in long, glistening, violet needles, melts at 100°, and on treatment with alcohol is converted into the pentaiodide. The *hexaiodidemonobromide*, $C_{18}H_{24}N_3I,I_5Br$, formed by the action of iodine on the hydrobromide, crystallises in long, black leaflets, is easily soluble in alcohol, and decomposes in a vacuum with loss of halogen. G. Y.

[Action of Iodine on Hydrazines.] Robert Stollé (*J. pr. Chem.*, 1902, [ii], 66, 332—338).—See this vol., ii, 100.

Action of Boron Trichloride on Phenylhydrazine. RICHARD ESCALES and GEORG KLING (*Ber.*, 1902, **35**, 4178. Compare Michaelis and Oster, Abstr., 1892, 1326).—The compound described by Michaelis and Oster as an additive product of phenylhydrazine and boron trichloride is presumably the hydrochloride of phenylhydrazine, as boron trichloride is decomposed by phenylhydrazine in ethereal solution, yielding a precipitate of the hydrochloride of the base decomposing at 243—246°. Michaelis and Oster give 242° for their compound.

J. J. S.

Action of Phenylhydrazine on the Oxygen Compounds of Selenium and Tellurium. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, **32**, 257—259).—An aqueous solution of tellurium dioxide gives, with phenylhydrazine, a yellowish precipitate, which, however, is very unstable, and reduction to tellurium quickly takes place.

When an alcoholic solution of phenylhydrazine is slowly added to a concentrated solution of selenic acid in alcohol, a precipitate is formed, and, on recrystallising from aqueous alcohol, silky needles of *phenylhydrazine selenate*, $(NHPh{\cdot}NH_2)_2,H_2SeO_4$, are obtained. This salt is stable in dry air.

J. McC.

Oxidation of Aldehyde-phenylhydrazones to α-Diketoneosazones. HEINRICH BILTZ and FRITZ SIEDEN (*Annalen*, 1902, **324**, 310—328. Compare Abstr., 1902, i, 467, 468).—Benzaldehyde-*p*-bromophenylhydrazone (m. p. 127·5°) is not converted into an osazone by aërial oxidation. *p*-Bromophenylbenzilosazone is, however, obtained directly by condensing benzil and *p*-bromobenzaldehyde in boiling acetic acid; it crystallises from benzene and alcohol in yellow needles melting at 233°; the intermediate hydrazone was not isolated.

Salicylaldehyde-p-*bromophenylhydrazone*, which is prepared by mixing its generators in alcoholic solution, melts at 175·5°, and, when oxidised by a current of air passed through its solution in dilute alcoholic potassium hydroxide, it yields a mixture of two isomeric osazones, these substances being separated by their different solubilities in nitrobenzene.

(*a*)-p-*Bromophenyldi*-o-*hydroxybenzilosazone* is readily soluble in chloroform or nitrobenzene, but dissolves very sparingly in alcohol, light petroleum, or water; it crystallises in yellowish-white prisms and melt at 233°. (*β*)-p-*Bromophenyldi*-o-*hydroxybenzilosazone* is sparingly soluble in nitrobenzene and practically insoluble in all the other solvents; it melts at 282°. The α-osazone yields a *triacetyl* derivative crystallising in rectangular prisms melting at 156°; the β-osazone, on the other hand, furnishes a *tetra-acetyl* derivative which separates from alcohol in white, hexagonal plates and melts at 233°; these substances are both produced by the action of acetic anhydride, the yield being increased by adding dry sodium acetate.

Vanillaldehyde-p-*bromophenylhydrazone*, produced from its generators in alcoholic solution, crystallises in rhombic plates melting at 145°; on aërial oxidation in the presence of a solution of potassium hydroxide in dilute alcohol, it yields p-*bromophenylvanillilosazone*, which crystal-

lises in pale yellow prisms, decomposes at 165°, and gives rise to a triacetyl derivative melting at 201°.

Benzaldehyde-*p*-nitrophenylhydrazone melts at 192—193° (compare Hyde, Abstr., 1899, i, 688), and when subjected to atmospheric oxidation it is hydrolysed and partly destroyed, so that no osazone is obtained; this negative result is likewise obtained with *salicylaldehyde*-p-*nitrophenylhydrazone*, a compound crystallising from alcohol in reddish-brown prisms melting at 227°.

Vanillaldehyde-p-*nitrophenylhydrazone* crystallises from glacial acetic acid in hexagonal plates melting at 227°; when oxidised by the method indicated, it yields p-*nitrophenylvanillilosazone*, a substance crystallising from nitrobenzene in small, yellowish-red needles melting at 247°; its *triacetyl* derivative, which is readily soluble in the ordinary organic solvents, melts at 230°.

Salicylaldehyde-p-*phenylmethylhydrazone*, prepared by mixing salicylaldehyde with a hot alcoholic solution of phenylmethylhydrazone hydrochloride, crystallises from alcohol in rectangular leaflets melting at 142°; it yields, on oxidation, a mixture of two isomeric osazones, one of which is labile and convertible into the other. The stable p-*phenylmethyldi*-o-*hydroxybenzilosazone* melts at 266° and is obtained from the crude product by crystallisation from glacial acetic acid; on acetylation with acetic anhydride and sodium acetate, it gives a *tetra-acetyl* derivative crystallising in colourless prisms and melting at 228°.

The labile osazone is obtained by passing carbon dioxide into the alkaline solution of the oxidation product; it melts at 243—255° and is not readily purified by crystallisation, since it changes into the stable isomeride even at 100°.

The condensation products of phenylhydrazine-*p*-sulphonic acid and the aromatic aldehydes (Abstr., 1902, i, 571) do not yield osazones on oxidation.

The results in this and previous communications indicate the influence of substituent radicles on the behaviour of the aromatic phenylhydrazones towards atmospheric oxygen. The presence of acidic radicles in the aldehyde complex and alkyl groups in the hydrazine residue renders the hydrazones less susceptible to hydrolysis, and therefore more capable of yielding osazones by oxidation. On the other hand, hydrazones containing acidic radicles in the hydrazine complex or alkyl groups in the aldehydic nucleus are more readily hydrolysed, this reaction preceding the oxidation, with the result that osazones are not obtained. G. T. M.

Phenylhydrazones of Hydroxyaldehydes. O. Anselmino (*Ber.*, 1902, 35, 4099—4108).—o-*Homosalicylaldehydephenylhydrazone*, $C_{14}H_{14}ON_2$, crystallises from light petroleum in rhombic plates. m-*Homosalicylaldehydephenylhydrazone* exists in two forms, of which one crystallises from light petroleum in silvery needles and melts at 136°; by boiling with alcohol, it is converted into the other form, which crystallises in yellow leaflets and melts at 168°. p-*Homosalicylaldehydephenylhydrazone* crystallises from alcohol in straw-yellow needles and melts at 149°. m-p-*Dimethylsalicylaldehydephenylhydrazone* crystallises

from alcohol in small, bright yellow, felted needles and melts at 190°; o-p-*dimethylsalicylaldehydephenylhydrazone* separates from light petroleum in small, hard aggregates and melts at 105°; p-*dimethylsalicylaldehydephenylhydrazone* crystallises from absolute alcohol in pale yellow plates and melts at 148°. The *phenylhydrazone* of 2 : 4 : 5-trimethylsalicylaldehyde crystallises from alcohol in leaflets and from light petroleum in long, flat needles; it melts at 144°.

The *phenylhydrazones* of the *p*-hydroxytolualdehydes have the following properties: [CHO : OH : Me = 1 : 3 : 4], crystalline crust, decomposing at 147°; [CHO : OH : Me = 1 : 2 : 4], from dilute alcohol, flat, lustrous needles, melting and decomposing at 88°.

o-*Homosalicylaldehyde*-p-*bromophenylhydrazone* crystallises from light petroleum in silvery leaflets and melts at 108°. p-*Homosalicylaldehyde*-p-*bromophenylhydrazone* crystallises from alcohol in sulphur-yellow leaflets and melts and decomposes at 181°. The *diphenylhydrazone*, $C_{22}H_{22}ON_4$, of the dialdehyde from *p*-xylenol crystallises from alcohol in dark yellow prisms and melts and decomposes at 209°.

The *semicarbazones* of the three homosalicylaldehydes all crystallise from glacial acetic acid in slender needles; the *o*-compound melts and decomposes at 241°, the *m*-compound at 210°, and the *p*-derivative at 238°.

o-*Homosalicylaldehydeazine*, $(OH\cdot C_6H_3Me\cdot CH)_2N_2$, prepared from the aldehyde and hydrazine sulphate, crystallises from glacial acetic acid in golden, lustrous needles and melts at 229°.

p-Homosalicylaldehydephenylhydrazone, $[Me : OH : CH\cdot N_2HPh = 1 : 4 : 3]$, dissolves in hot acetic anhydride, giving the *diacetyl* derivative, $OAc\cdot C_6H_3Me\cdot CH\colon N\cdot NPhAc$, which crystallises from alcohol in snow-white, felted needles and melts at 149°; the *monoacetyl* derivative, $OH\cdot C_6H_3Me\cdot CH\colon N\cdot NPhAc$, is obtained from the latter by boiling it with alcoholic potassium hydroxide, and crystallises from light petroleum in short needles melting at 126°. The *benzoyl* derivative, $OBz\cdot C_6H_3Me\cdot CH\colon N\cdot NHPh$, of the phenylhydrazone is obtained by treatment with benzoyl chloride in pyridine according to the Einhorn-Hollandt method; it crystallises from alcohol in golden-yellow, vitreous prisms, melts at 161°, and with acetic anhydride gives the *acetylbenzoyl* compound,

$$OBz\cdot C_6H_3Me\cdot CH\colon N\cdot NPhAc,$$

melting at 140°, which, on hydrolysis, again gives the foregoing acetyl derivative melting at 126°. The *dibenzoyl* derivative of the phenylhydrazone crystallises from methyl alcohol in white needles, melts at 164°, and on hydrolysis gives rise to the *monobenzoyl* derivative,

$$OH\cdot C_6H_3Me\cdot CH\colon N\cdot NPhBz,$$

which melts at 155°.

o-p-*Dimethylsalicylaldehyde* is only obtained in small quantity from *as*-*m*-xylenol by Reimer's reaction, it melts at 11° and boils at 222° (uncorr.). *p*-Xylenol, when subjected either to Reimer's or Gatterman's reaction, preferably the latter, gives a small quantity (5 per cent.) of the o-*hydroxyaldehyde*, $[Me_2 : OH : CHO = 1 : 4 : 2 : 3]$, only a small, quantity of the *p*-hydroxyaldehyde being formed in Reimer's reaction.

It is noteworthy that the phenylhydrazones of *o*-hydroxyaldehydes, although containing phenolic hydroxyl radicles, are insoluble in dilute

alkalis and fail to yield alkyl ethers when boiled with methyl iodide and sodium in methyl alcoholic solution; the presence of this group is, however, shown by the formation of the foregoing acetyl and benzoyl derivatives. The phenylhydrazones of *p*-hydroxyaldehydes are normal in their behaviour, as are also the semicarbazones and azines of both *o*- and *p*-hydroxyaldehydes. W. A. D.

Glyoxalines. ADOLF PINNER (*Ber.*, 1902, 35, 4131—4142).—Phenylglyoxal, COPh·CHO, can be prepared from *iso*nitrosoacetophenone by the action of sodium hydrogen sulphite and then of dilute sulphuric acid (Müller and von Pechmann, Abstr., 1890, 51), provided the solid sulphite is used. If the commercial solution, containing free sulphurous acid, is employed, an *acid*, $C_{16}H_{12}O_4N_2S$, is produced, which crystallises from hot 5 per cent. sulphuric acid in anhydrous, yellowish needles, and from the cold solution in colourless, efflorescent plates with $4H_2O$. The *ammonium* salt,

$$C_{16}H_{11}O_4N_2S{\cdot}NH_4,2H_2O,$$

forms slender, sparingly soluble needles and is only slowly dehydrated at 120°. The basic *lead* salt, $C_{16}H_{11}O_4N_2S{\cdot}Pb{\cdot}OH$, forms yellow needles and is only slightly soluble in water, but dissolves very readily in acetic or nitric acid. The *silver* salt, $C_{16}H_{11}O_4N_2SAg$, forms white needles and is not sensitive to light. It is suggested that the first product of the reaction is the sulphonic acid, $CH_2Ph{\cdot}NH{\cdot}SO_3H$, which then condenses with a second molecule of *iso*nitrosoacetophenone to form *2-benzoyl-5-phenylglyoxaline-1-sulphonic acid*, $\begin{matrix}N{=}CBz\\ |\ \ \ \ \ \ \ \ \\ CH{:}CPh\end{matrix}\!\!>\!N{\cdot}SO_3H$.

By the action of ammonia on phenylglyoxal, Müller and von Pechmann obtained a compound to which they assigned the formula $C_{22}H_{17}ON_3$ or $C_{22}H_{19}ON_3$; this is now shown to be identical with a compound, $C_{16}H_{12}ON_2$, which Engler and Hassenkamp (Abstr., 1885, 1223) obtained by the action of ammonia on dibromoacetophenone, $C_6H_5{\cdot}CO{\cdot}CHBr_2$; the latter formula for the compound has been confirmed, and it is regarded as *2-benzoyl-5-phenylglyoxaline*,

$$\begin{matrix}N{=}CBz\\ |\ \ \ \ \ \ \ \ \\ CH{:}CPh\end{matrix}\!\!>\!NH,$$

the parent substance of the sulphonic acid just described; the melting point of the compound is given as 194—195°.

5-Phenylglyoxaline, $\begin{matrix}N{=}CH\\ |\ \ \ \ \ \ \ \ \\ CH{:}CPh\end{matrix}\!\!>\!NH$, prepared from phenylglyoxal, formaldehyde, and ammonia, crystallises from water in glistening flakes and melts at 128—129°. The *platinichloride*, $(C_9H_8N_2)_2,H_2PtCl_6,3H_2O$, forms stout, orange-red prisms, loses $2H_2O$ at 120°, and melts and completely decomposes at 215°.

Diphenylglyoxaline hydrochloride, $C_{15}H_{12}N_2,HCl$, forms efflorescent, glistening flakes and melts at 202°. *4:5-Diphenyl-1-methylglyoxaline*, $\begin{matrix}N{=}CH\\ |\ \ \ \ \ \ \ \ \ \ \\ CPh{:}CPh\end{matrix}\!\!>\!NMe$, prepared from diphenylglyoxaline and methyl iodide, separates from dilute alcohol in glistening crystals and melts at 147°.

Triphenylglyoxaline (lophine) can be very readily and very effectively purified by crystallising from pyridine and washing the product with alcohol. Methyl sulphate forms an *additive* compound with lophine, $C_{21}H_{16}N_2,Me_2SO_4,2H_2O$, which separates from alcohol in glistening, efflorescent prisms, sinters at 80°, and, when dry, melts with frothing at 115—117°. This compound is very stable, is not altered by boiling with alcohol or with dilute aqueous hydrogen chloride, and only yields sulphuric acid when boiled with concentrated nitric acid. Diphenylglyoxaline appeared to form a similar compound, but this could not be isolated, and on adding water hydrolysis took place and the *acid sulphate*, $C_{15}H_{12}N_2,H_2SO_4$, was precipitated.

T. M. L.

Bromination of Benziminoazoles. WL. BACZYŃSKI and STEFAN VON NIEMENTOWSKI (*Bull. Acad. Sci. Cracow*, 1902, 421—435).—The experimental proof that the bromine compounds of benziminoazole contain two bromine atoms in the iminoazole ring at the position of the double linking between the nitrogen and carbon atoms has involved the preparation of the following compounds (compare Abstr., 1898, i, 337).

6-Bromo-2-methylbenziminoazole, $C_6H_3Br{<}{\genfrac{}{}{0pt}{}{N}{NH}}{>}CMe$ (compare Remmers, Abstr., 1874, 696), prepared by the reduction of *p*-bromo-*o*-nitroacetanilide with stannous chloride and hydrochloric acid, melts at 218°. The *hydrochloride* crystallises with $1H_2O$ in plates and melts and decomposes at 260°. The *nitrate* forms needles and decomposes at 212°. The *platinichloride* crystallises with $2H_2O$ in orange-yellow needles and melts and decomposes at 260°; the *aurichloride* crystallises with $1H_2O$ in yellow needles and melts at 237°. 5 : 7-*Dibromo-2-methyloxybenziminoazole*, $C_6H_2Br_2{<}{\genfrac{}{}{0pt}{}{N}{NH\cdot CMe}}{>}O$, prepared by the reduction of dibromo-*o*-nitroacetanilide, crystallises in rhombic plates, softens at 255°, melts at 269°, is very sparingly soluble in organic solvents, and forms a *potassium* salt, $C_8H_5ON_2Br_2K$. The *hydrochloride* crystallises in needles; the *nitrate* in pale yellow plates. 5 : 7-*Dibromo-2-methylbenziminoazole*, $C_6H_2Br_2{<}{\genfrac{}{}{0pt}{}{N}{NH}}{>}CMe$, crystallises in leaflets, softens at 230°, and melts at 236°. The *hydrobromide* forms leaflets and the *nitrate* white needles.

The *tetrabromo*-compound, $C_6H_3Br{<}{\genfrac{}{}{0pt}{}{NBr}{NH}}{>}CMeBr,HBr$, prepared by the action of bromine (2 mols.) on 2-methylbenziminoazole (1 mol.) dissolved in glacial acetic acid, forms orange crystals, melts at 163°, and on slowly heating loses its colour and yields a white hydrobromide. The orange *pentabromo*-compound, $C_6H_2Br_2{<}{\genfrac{}{}{0pt}{}{NBr}{NH}}{>}CMeBr,HBr$, obtained by the action of bromine on 6-bromo-2-methylbenziminoazole or 4-bromo-2-methylbenziminoazole, forms, on heating, a white substance which does not melt even at 270°. By the action of bromine on tribromo-2-methylbenziminoazole, an orange-red *hexabromo*-com-

pound, $C_6HBr_3{<}\substack{NBr\\NH}{>}CMeBr,HBr$, is obtained. The preceding bromine compounds are stable at the ordinary temperature and are quickly decomposed by water, potassium iodide, benzene, or aniline, forming, as a rule, bromo-derivatives containing bromine in the benzene ring.

4-*Bromo-2-methylbenziminoazole*, $C_6H_3Br{<}\substack{-N-\\NH}{>}CMe$, is formed either by boiling the tetrabromo-compound with anhydrous benzene or aniline, by treating it with an aqueous solution of potassium iodide, by allowing 2-methylbenziminoazole to remain with a solution of bromine (1 mol.) in glacial acetic acid, or by the reduction of 4 : 6-dibromo-2-methylbenziminoazole with zinc and glacial acetic acid; it crystallises in leaflets, melts at 210—211°, is very readily soluble in alcohol or ether, less so in boiling water or alkali hydroxides, and is precipitated from its solution in alkalis by carbon dioxide. By the prolonged action of zinc dust and glacial acetic acid, it is reconverted into 2-methylbenziminoazole. The *hydrochloride*, $C_8H_7N_2Br,HCl,H_2O$, crystallises in white leaflets, the *nitrate* in needles, and the *platinichloride*, $(C_8H_7N_2Br)_2,H_2PtCl_6,H_2O$.

4 : 6-*Dibromo-2-methylbenziminoazole*, $C_6H_2Br_2{<}\substack{NH\\-N-}{>}CMe$, prepared by the action of water on the tetrabromo-compound, by treating the pentabromo-compound with benzene or potassium iodide solution, or by the action of bromine (2 mols.) on 2-methylbenziminoazole, crystallises in white needles, melts at 238°, is readily soluble in alcohol, very sparingly so in ether, and insoluble in water; it is precipitated from its solutions in alkali hydroxides by carbon dioxide. By the action of zinc and glacial acetic acid, it yields 4-bromo-2-methylbenziminoazole. The *hydrochloride*, $C_8H_6N_2Br_2,HCl$, *hydrobromide*, $C_8H_6N_2Br_2,HBr,3H_2O$, the *nitrate*, $C_8H_6N_2Br_2,2HNO_3$, and the *platinichloride*, $(C_8H_6N_2Br_2)_2,H_2PtCl_6$, have been prepared.

2 : 4 : 7-*Tribromo-2-methylbenziminoazole*, $C_6HBr_3{<}\substack{NH\\-N-}{>}CMe$, obtained either by the action of water on the pentabromo-compound or by the bromination of 4 : 6-dibromo-2-methylbenziminoazole, forms white crystals, melts at 273—278°, is slightly soluble in hot alcohol, very sparingly so in ether, insoluble in water, and is precipitated from its solutions in alkalis by carbon dioxide. By the prolonged action of zinc dust and glacial acetic acid, it forms 4-bromo-2-methylbenziminoazole. The *hydrochloride*, $C_8H_5N_2Br_3,HCl,H_2O$, and *nitrate*, $C_8H_5N_2Br_3,HNO_3$, crystallise in white needles.

4 : 5 : 6 : 7-*Tetrabromo-2-methylbenziminoazole*, $C_6Br_4{<}\substack{NH\\-N-}{>}CMe$, prepared either by boiling the orange-coloured hexabromo-compound with water or by brominating 2-methylbenziminoazole or one of its bromo-substitution products, separates in white, crystalline granules, melts at 317°, is very sparingly soluble in organic solvents, insoluble in water, and is precipitated from its solutions in alkali hydroxides by carbon dioxide. The *hydrochloride*, $C_8H_4N_2Br_4,HCl$, and the *nitrate*, $C_8H_4N_2Br_4,HNO_3$,

crystallise in white needles and melt at 278—280° and 313° respectively.

In order to determine whether the bromine in the preceding derivatives is really contained in the benzene ring, the phthalones and benzylidene derivatives were prepared from 4 : 6-dibromo-2-methylbenziminoazole and tetrabromo-2-methylbenziminoazole, and these compounds were again oxidised to dibromo- and tetrabromo-benziminoazole.

The *phthalone* of 4 : 6-*dibromo-2-methylbenziminoazole*,

$$C_6H_2Br_2<{NH \atop N}>C\cdot CH<{CO \atop CO}>C_6H_4,$$

prepared by heating a mixture of methyldibromobenziminoazole and phthalic anhydride at 250°, crystallises in microscopic, orange-yellow needles and small plates, does not melt below 370°, and is insoluble in most organic solvents; it forms a reddish solution in concentrated sulphuric acid and is precipitated in yellow flakes on the addition of water. The *phthalone* of *tetrabromo-2-methylbenziminoazole*,

$$C_6HBr_4<{NH \atop N}>C\cdot CH<{CO \atop CO}>C_6H_4,$$

melts and becomes black at about 270° and resembles the preceding compound. 2-*Benzylidene*-4 : 6-*dibromo-2-benzylidenemethylbenziminoazole*, $C_6H_2Br_2<{NH \atop N}>C\cdot CH:CHPh$, prepared by heating dibromomethylbenziminoazole with benzaldehyde at 200°, crystallises from alcohol in pale yellow needles containing $\frac{1}{2}H_2O$, melts at 182—186°, is soluble in alcohol or ether but insoluble in water, and on oxidation with potassium permanganate yields 4 : 6-*dibromobenziminoazole*,

$$C_6H_2Br_2<{NH \atop N}>CH,$$

which crystallises in white plates containing H_2O, melts at 225°, and is soluble in alcohol, very sparingly so in ether, and insoluble in water. *Tetrabromo-2-benzylidenemethylbenziminoazole*,

$$C_6Br_4<{NH \atop N}>C\cdot CH:CHPh,$$

forms small, pale yellow plates, crystallises with H_2O, melts at 240—246°, and is rather sparingly soluble in alcohol or ether and insoluble in water; on oxidation with potassium permanganate, it forms *tetrabromobenziminoazole*, $C_6Br_4<{NH \atop N}>CH$, which crystallises in small, pale yellow prisms, melts at 339°, and is soluble in acetone, sparingly so in alcohol, still less soluble in ether, and insoluble in water. E. W. W.

Naphthacrihydridine. RICHARD MÖHLAU and O. HAASE (*Ber.*, 1902, **35**, 4164—4172. Compare Morgan, Trans., 1898, **73**, 536).—The compound described by Morgan as *iso*naphthacridine is shown to have the double molecular formula and to be *naphthacrihydridine*, $CH<{C_{10}H_6 \atop C_{10}H_6}>NH\cdot N<{C_{10}H_6 \atop C_{10}H_6}>CH_2$. Although the molecular weight cannot be determined by the usual methods, its characteristic properties and its relationship to naphthacridine support the constitution ascribed to it by the authors. It melts at 235—236°, not 225—226°.

Methylene-β-naphthylamine, $C_{10}H_7N{:}CH_2$, obtained by the action of formaldehyde solution on a cold acetic acid solution of β-naphthylamine and precipitated by pouring into a 1 per cent. solution of sodium chloride, melts at 62—64°, is sparingly soluble in alcohol or ether, but readily soluble in other organic solvents. When boiled with mineral acids, it is hydrolysed and yields formaldehyde. It readily undergoes polymerisation when warmed with any solvent; the product, which crystallises in colourless, six-sided plates, melts at 203° and appears to be identical with Morgan's dimethylenediaminodinaphthylmethane.

Methylenedi-β-naphthylamine, $CH_2(NH{\cdot}C_{10}H_7)_2$, obtained by the action of aqueous formaldehyde on a hot acetone solution of β-naphthylamine, crystallises from alcohol in colourless needles melting at 104°. It dissolves in dilute acids and in most organic solvents; its ethereal solution has a dark blue fluorescence and solutions of its salts have an azure-blue fluorescence. J. J. S.

Syntheses with Phenylazoimide. Otto Dimroth (*Ber.*, 1902, **35**, 4041—4060. Compare Abstr., 1902, i, 403).—As in the case of ethyl acetoacetate, phenylazoimide is able to condense with ethyl benzoylacetate, ethyl malonate, ethyl methylacetoacetate, ethyl acetate, ethyl propionate, ethyl cyanoacetate, and benzyl cyanide, forming 1 : 2 : 3-triazole derivatives.

The constitution of these triazole compounds has been demonstrated; the phenyltriazolonecarboxylic acid obtained from ethyl malonate, when boiled with hydrochloric acid, yields the anilide of chloroacetic acid, nitrogen, and carbon dioxide, and therefore has the constitution $NPh<\begin{matrix}N=N\\ CO{\cdot}CH{\cdot}CO_2H\end{matrix}$; further, hydroxyphenylmethyltriazole, prepared from ethyl propionate, is oxidised to the anilide of pyruvic acid and accordingly has the constitution $NPh<\begin{matrix}N=\!=N\\ C(OH){:}CMe\end{matrix}$.

[With Eugen Letsche.]—1 : 5-*Diphenyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, $NPh<\begin{matrix}N=N\\ CPh{:}C{\cdot}CO_2H\end{matrix}$, is prepared by treating ethyl benzoylacetate and phenylazoimide (mol. proportions) with sodium (1 mol.) dissolved in alcohol; it crystallises in slender needles melting at 164—165°; the *sodium* salt crystallises with $3{\cdot}5H_2O$ in needles, the *barium* salt with $5H_2O$ in small needles, and the insoluble *copper* salt with $1{\cdot}5H_2O$ in pale blue, slender needles; the *methyl* ester forms small crystals melting at 135—136° and the *ethyl* ester long needles melting at 134—135°. 1 : 5-*Diphenyl*-1 : 2 : 3-*triazole*, $NPh<\begin{matrix}N=N\\ CPh{:}CH\end{matrix}$, is prepared by heating the corresponding acid at 170—175°; it crystallises in small, white plates melting at 113—114° and has feebly basic properties, yielding a *hydrochloride* when hydrogen chloride is passed into a dry ethereal solution.

[With Ernst Eberhardt.]—*Methyl* 1-*phenyl*-5-*triazolone*-4-*carboxylate*, $NPh<\begin{matrix}N=N\\ CO{\cdot}CH{\cdot}CO_2Me\end{matrix}$, is obtained as the sodium derivative by mixing

mol. proportions of phenylazoimide and methyl sodiomalonate in methyl alcoholic solution; the ester is obtained from the sodium derivative by treating its aqueous solution with fuming hydrochloric acid; it crystallises in yellow prisms or rhombohedra melting at 82—83° and is insoluble in dilute sodium hydroxide. When suspended in, or heated with, aqueous sodium hydroxide, it is converted into the enolic form, *methyl* 5-*hydroxy*-1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxylate*,

$$NPh<\begin{matrix}N\!=\!\!=\!\!=\!N\\ C(OH){:}C\cdot CO_2Me\end{matrix},$$

which can be prepared by cautious addition of hydrochloric acid to the pure sodium salt; the latter is obtained by treating the above ketonic compound with the calculated quantity of sodium dissolved in methyl alcohol; this salt dissolves with a neutral reaction in water; the enolic ester crystallises in small crystals with H_2O and, when anhydrous, melts at 72—73°; it has an acid reaction and can be titrated in the presence of phenolphthalein; in alcoholic solution it gives, with ferric chloride, a brownish-red coloration, whereas the ketonic form gives none. When the enolic ester is boiled with water or in solution in organic solvents, it is very largely, but not completely, transformed into the ketonic ester; when an alcoholic solution of the latter is boiled, it is changed, to a certain extent, into the enolic form.

Ethyl 1-*phenyl*-5-*triazolone*-4-*carboxylate*, $NPh<\begin{matrix}N\!=\!N\\ CO\cdot CH\cdot CO_2Et\end{matrix}$, prepared from ethyl malonate, crystallises in yellowish, prismatic needles melting at 73—74° and insoluble in sodium hydroxide; when treated with sodium ethoxide, it is converted into the *sodium* salt of the *enolic ester*; the latter forms white needles, is soluble in alkalis, and gives a coloration with ferric chloride. 1-*Phenyl*-5-*triazolone*-4-*carboxylic acid* is prepared by hydrolysing either the ketonic or enolic esters with sodium hydroxide; it crystallises in yellow needles melting and decomposing at 111—112°; when boiled with water, the acid decomposes with evolution of carbon dioxide; it is converted into the anilide of chloroacetic acid on boiling with fuming hydrochloric acid. The enolic form, 5-*hydroxy*-1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, is obtained from the disodium salt by cautious treatment with fuming hydrochloric acid; it crystallises with H_2O in white leaflets melting at 82—83°; it gives a brownish-red coloration with ferric chloride and is dibasic when titrated in the presence of phenolphthalein; it is converted into the ketonic-acid by dissolving in petroleum. The *dipotassium* salt, $C_9H_5O_3N_3K_2,2H_2O$, crystallises in white needles softening at 105°; the *monopotassium* salt, obtained from the preceding salt, is a crystalline powder which is acid to litmus and phenolphthalein.

5-*Hydroxy*-1-*phenyl*-1 : 2 : 3-*triazole*, $NPh<\begin{matrix}N\!=\!\!=\!N\\ C(OH){:}CH\end{matrix}$, prepared by heating the enolic acid in aqueous solution, is a crystalline powder melting at 118—119° and gives a brownish-red coloration with ferric chloride; it is also obtained by the action of phenylazoimide on ethyl acetate.

[With Eugen Letsche.]—Phenylazoimide and ethyl methylacetoacetate react violently in the presence of sodium ethoxide, giving,

with the elimination of ethyl acetate, 5-*hydroxy*-1-*phenyl*-4-*methyl*-1 : 2 : 3-*triazole*, which forms white needles decomposing at 133—134°, is soluble in alkalis, and gives a coloration with ferric chloride. The *sodium* salt crystallises with $2H_2O$ in needles and the *potassium* salt in leaflets. This triazole also has basic properties and forms a *hydrochloride* which crystallises in needles with H_2O, melting at 138—139°; the anhydrous *hydrochloride* forms large plates. On oxidation, this triazole yields the anilide of pyruvic acid. With phenylazoimide, ethyl methylmalonate or ethyl propionate also gives this triazole.

[With G. Werner.]—Phenylazoimide and benzyl cyanide condense in the presence of sodium ethoxide, forming 5-*amino*-1 : 4-*diphenyl*-1 : 2 : 3-*triazole*, $NPh\langle\begin{matrix}N{=\!=\!=}N\\ C(NH_2){:}\overset{|}{C}Ph\end{matrix}$, which forms white crystals melting at 169°; it is a weak base and yields a crystalline *hydrochloride*; the *acetyl* derivative forms prismatic crystals melting at 172°; the *benzylidene* compound forms small, yellow leaflets melting at 175°.

Ethyl cyanoacetate and phenylazoimide give *ethyl* 5-*amino*-1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, $NPh\langle\begin{matrix}N{=\!=\!=}N\\ C(NH_2){:}\overset{|}{C}{\cdot}CO_2Et\end{matrix}$, which crystallises in white needles melting at 122°; the *acetyl* derivative crystallises in leaflets melting at 81°. 5-*Amino*-1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* is obtained by hydrolysing the ester with alcoholic potassium hydroxide; it forms small crystals melting at 142°; the *potassium* salt crystallises in needles. 5-*Amino*-1-*phenyl*-1 : 2 : 3-*triazole* is obtained by heating the acid a few degrees above its melting point; it forms crystals melting at 139°. K. J. P. O.

Ring Condensations of the Esters of Uramido- and Semicarbazino-Acids with Sodium Ethoxide. James R. Bailey [and, in part, C. P. Norby, S. F. Acree, and M. B. Wesson] (*Amer. Chem. J.*, 1902, **28**, 386—403).—The *amide* of hydantoic acid melts and decomposes at 204°. The nitrile may be prepared by the action of potassium cyanate on the hydrochloride of glycine nitrile; it crystallises in prisms and melts at 139°.

Ethyl lacturamidate, $NH_2{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2Et$, obtained by the action of potassium cyanate on the hydrochloride of ethyl hydantoate, crystallises from benzene in slender needles, melts at 100°, and is readily soluble in water, chloroform, or alcohol. When sodium ethoxide is added to an alcoholic solution of this substance, the sodium derivative of lactylcarbamide is produced; lactylcarbamide, when crystallised from a mixture of alcohol and ether, melts at 148°.

Ethyl γ-phenylhydantoate, $NHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, prepared by the action of phenylcarbimide on the hydrochloride of the ethyl ester of glycine, crystallises in slender needles and melts at 108—109°; it reacts with sodium ethoxide with formation of γ-phenylhydantoin. *γ-Phenylhydantoic acid*, obtained by boiling γ-phenylhydantoin with solution of barium hydroxide, crystallises in slender needles and melts and decomposes at 197°.

Propyl semicarbazinopropionate (propyl carbonamidohydrazopropion-

ate), prepared by the action of propyl alcohol and hydrochloric acid on the nitrile (Thiele and Bailey, Abstr., 1899, i, 169), melts at 89° and is converted by potassium permanganate into the *semicarbazone* of propyl pyruvate, $NH_2\cdot CO\cdot NH\cdot N:CMe\cdot CO_2Pr$, melting at 178°. *Methyl semicarbazinopropionate* crystallises from benzene in slender prisms, melts at 100°, and is converted by potassium permanganate into a *semicarbazone*, $C_5H_{11}O_3N_3$, which melts and decomposes at 208°.

3 : 5-Dihydroxy-6-methyl-1 : 6-dihydro-1 : 2 : 4-triazine,

$$NH<\begin{matrix}N{=\!=}C(OH)\\CHMe\cdot C(OH)\end{matrix}>N$$

(Abstr., 1899, i, 169), is obtained by the condensation of ethyl semicarbazinopropionate, which may be effected by the action of mineral acids, of heat, of alcoholic potassium hydroxide, or of sodium ethoxide on it; the *sodium* salt was prepared and analysed. When the triazine is boiled with barium hydroxide solution, it is converted into semicarbazinopropionitrile. The corresponding 1-*benzoyltriazine*, obtained by the action of sodium ethoxide on ethyl benzoylsemicarbazinopropionate, melts at 201°, solidifies at about 180°, and then melts at 210°; it crystallises from hot alcohol in short, microscopic prisms; when heated with solution of potassium hydroxide, it is converted into 3-hydroxy-5-phenyltriazole-1-propionic acid (Bailey and Acree, Abstr., 1900, i, 528).

*Semicarbazino*iso*butyric acid*, $NH_2\cdot CO\cdot NH\cdot NH\cdot CMe_2\cdot CO_2H$, prepared by boiling semicarbazinobutyramide with barium hydroxide, crystallises in cubes and melts and decomposes at 194°; the *methyl* and *ethyl* esters melt at 106·5° and 97° respectively.

3 : 5-*Dihydroxy*-6-*dimethyl*-1 : 6-*dihydro*-1 : 2 : 4-*triazine*,

$$NH<\begin{matrix}N{=\!=}C(OH)\\CMe_2\cdot C(OH)\end{matrix}>N,$$

obtained by the action of sodium ethoxide on ethyl semicarbazino*iso*butyrate, crystallises from alcohol in thin plates and melts at 230°.

E. G.

Action of Hydrazine on Thiamines. Alfred Junghahn and J. Bunimowicz

(*Ber.*, 1902, 35, 3932—3940. Compare Abstr., 1898, i, 337).—Thio-β-naphthoamide is converted by hydrazine hydrate into the β-dinaphthyldihydrotetrazine previously described by Pinner. Thio-α-naphthoamide yields a very small amount of a substance which is probably the corresponding dihydrotetrazine derivative, and yields a red oxidation product melting at 185°.

m-Aminothiobenzamide is best prepared by reducing *m*-nitrobenzonitrile with ammonium sulphide and heating the resulting oil with alcoholic ammonium sulphide at 100° under pressure; it crystallises in pale yellow plates melting at 139°. Hydrazine hydrate converts it into a mixture of substances; one of these contains sulphur, crystallises in pale yellow needles melting at 239—240°, and forms a crystalline hydrochloride. This is probably produced by the action of the hydrogen sulphide generated in the reaction on the diaminodibenzenylhydrazidine which is the first product, and possibly has the constitution $NH_2\cdot C_6H_4\cdot C<\begin{matrix}S\\N\cdot N\end{matrix}>C\cdot C_6H_4\cdot NH_2$.

Di-m-*aminodiphenyldihydrotetrazine*,

$$NH_2\cdot C_6H_4\cdot C\Big\langle\begin{matrix}NH\cdot HN\\ N\text{——}N\end{matrix}\Big\rangle C\cdot C_6H_4\cdot NH_2,$$

is also formed in the foregoing reaction, and crystallises in yellow needles melting at 179—190°. Oxidation converts it into *di*-m-*aminodiphenyltetrazine*, which is also formed in small amount along with the dihydro-compound, and crystallises in red needles melting at 266—267°. The *nitrate* crystallises with $3H_2O$ in reddish needles, the *sulphate* forms red plates, and the *hydrochloride* needles. *Diacetyl*-m-*diaminodiphenyltetrazine* crystallises in slender, violet needles melting at 295°.

p-*Aminophenylthioacetamide* is prepared by the reduction of *p*-nitrobenzyl cyanide with ammonium sulphide and forms light yellow crystals melting at 173°. Hydrazine hydrate converts it into *di*-p-*aminodibenzyldihydrotetrazine*, which crystallises in colourless needles melting at 212°. Ferric chloride oxidises it to *di*-p-*aminodibenzyltetrazine*, $C_{16}H_{16}N_6$, which crystallises in lustrous, red plates melting at 166°, the *diacetyl* compound forms violet needles melting at 205°. When di-*p*-aminodibenzyldihydrotetrazine is diazotised, oxidation occurs and a diazo-compound of the tetrazine base is formed, which unites with *β*-naphthol forming an amorphous, red *azo*-compound, which can be recrystallised from acetic acid and decomposes at about 200°. A compound containing sulphur is also formed in the reaction between hydrazine hydrate and aminothioacetamide, and, by analogy with the derivative of aminothiobenzamide, probably has the constitution $NH_2\cdot C_6H_4\cdot CH_2\Big\langle\begin{matrix}\text{—S—}\\ N\cdot N\end{matrix}\Big\rangle C\cdot CH_2\cdot C_6H_4\cdot NH_2$; it crystallises in light yellow prisms melting at 148°. A. H.

Action of Zinc Ethyl on Diazobenzene Chloride. EUGEN BAMBERGER and MICH. TICHVINSKY (*Ber.*, 1902, 35, 4179—4190).—Phenyl-*aβ*-diethylhydrazine, *aa*-phenylethylhydrazine, and *s*-diethylbenzidine are the chief products obtained when finely divided diazobenzene chloride, moistened with ether, is added gradually to a solution of zinc ethyl in dry ether cooled to 15°.

Phenyl-aβ-diethylhydrazine, NEtPh·NHEt, is a colourless oil distilling at 111—115° under 12 mm. pressure; it dissolves readily in most organic solvents, is only sparingly soluble in water, and reduces Fehling's solution. Its *benzoyl* derivative, NEtPh·NEtBz, which crystallises from ether in glistening rhombohedra, softens at 58·5°, melts at 59—60°, and cannot be readily hydrolysed. The *nitrosoamine*, NEtPh·NEt·NO, is a yellow oil very sparingly soluble in water, and, on reduction with zinc dust and acetic acid, yields a *phenyldiethyltriazan*, $NEtPh\cdot NEt\cdot NH_2$ (?), the *oxalate* of which melts at 113·5—114·5° (corr.). When phenyldiethylhydrazine is reduced with sodium and alcohol, it is converted into ethylaniline and ethylamine. *aa*-Phenylethylhydrazine was isolated in the form of its *benzoyl* derivative melting at 167—168° and moderately soluble in light petroleum; the same benzoyl derivative is obtained when phenylethylnitrosoamine is reduced and the reduction product benzoylated.

s-*Diethylbenzidine*, $NHEt\cdot C_6H_4\cdot C_6H_4\cdot NHEt$, crystallises from light

petroleum or from alcohol in colourless plates melting at 115·5—116° to a turbid liquid which becomes clear at 120°. The crystals obtained from light petroleum, when dried on a porous plate, gradually assume a pale greenish-blue colour. An alcoholic solution of the base gives a deep green coloration with ferric chloride. The *nitrosoamine*, $C_2H_8(NEt\cdot NO)_2$, crystallises in straw-yellow, glistening plates and melts at 162·5—163·5°. The *diacetyl* derivative melts at 166·5—167·5, the *dibenzoyl* derivative at 184·5—185·5°, and is readily soluble in alcohol. When heated with concentrated hydrochloric acid at 250—260° for 9 hours, the base is converted into benzidine and ethyl chloride. On repeating P. W. Hofmann's synthesis of *s*-diethylbenzidine, the authors obtained a base identical with the one described above, melting at 116—120° and not at 65° (*Annalen*, 1860, **115**, 365).

J. J. S.

Replacement of the Diazo- by the Amino-group. LEONHARD WACKER (*Ber.*, 1902, **35**, 3920—3928. Compare Abstr., 1902, i, 698). —The diazotised heteronuclear diaminoanthraquinones react with ammonium and hydroxylamine salts in a similar manner to the monoamino-derivatives, the change occurring partly in one nucleus and partly in both, and the product consisting of a mixture of the resulting substances.

1-Aminoanthraquinone is prepared by reducing the nitro-compound with dextrose and alcoholic aqueous potash; the corresponding diazo-compound is converted by ammonium carbonate into anthraquinone-diazoamide, which is reconverted into the original amino-compound by boiling with dilute sulphuric acid. Hydroxylamine hydrochloride also reacts with the diazo-solution, forming the brownish-red *anthraquinone-diazohydroxyamide*, $C_{14}H_7O_2\cdot N\colon N\cdot NH\cdot OH$, and this is converted by sulphuric acid into 1 : 4-*aminohydroxyanthraquinone*, which forms a reddish-violet powder melting at 207—208°. The diazo-derivative of this substance is converted by boiling with an alkali into monohydroxy-anthraquinone, but if it is first combined with dimethylamine and the resulting compound heated with sulphuric acid, quinizarin is produced, the constitution of the 1 : 4-aminohydroxy-compound being thus established. The same compound can be obtained by the action of hydrazine on the diazo-compound. With ammonium chloride, 1 : 5-bisdiazoanthraquinone yields a substance which forms crystals having a bronze lustre and yielding a reddish-violet aqueous solution. When this compound is heated with sulphuric acid in presence of boric acid, it yields 1 : 5-diaminoanthraquinone together with 1 : 5-*aminohydroxyanthraquinone*, which crystallises in dark red needles melting at 215—216°. 1 : 5-Diaminoanthraquinone is also regenerated when 1 : 5-bisdiazoanthraquinone is treated with methylamine and the resulting yellow compound warmed with acetic acid. Dimethylamine, on the other hand, yields an unstable compound which is converted, by heating with sulphuric acid at above 170°, into anthrarufin. Hydroxylamine hydrochloride yields, with the bisdiazo-solution, a bordeaux-red precipitate which can be crystallised from water and detonates feebly when heated; it contains chlorine, but its exact composition has not yet been ascertained. When heated with a mixture of

sulphuric acid and boric acid, it yields a dark violet powder which is probably 1-*amino*-4 : 5-*dihydroxyanthraquinone*. Ammonia also reacts with 1 : 8-bisdiazoanthraquinone, forming a substance which, by treatment with sulphuric acid, is converted into 1 : 8-diaminoanthraquinone and 1 : 8-*aminohydroxyanthraquinone*; the latter forms a reddish-brown powder melting at 214—215°. With the 1 : 8-bisdiazo-solution, hydroxylamine hydrochloride also yields a compound, which is converted by sulphuric acid into a dark red powder, consisting probably of a mixture of 1-amino-4 : 8-dihydroxyanthraquinone with 1 : 8-diamino-4 : 5-dihydroxyanthraquinone. A. H.

Limits of the Formation of Diazoamino-compounds. Some Azo-dyes. STEFAN VON NIEMENTOWSKI [in part with CEZAR WICHROWSKI] (*Bull. Acad. Sci. Cracow*, 1902, 413—419. Compare Abstr., 1893, i, 201; 1897, i, 340).—Generally speaking, diazoamino-compounds are most readily formed from amino-compounds containing Cl, NO_2, CN, &c., groups; they are not readily obtained from the naphthylamines, and still smaller yields of diazoamino-compounds are obtained from the toluidines, *m*-xylidine, aminophenols, and aminobenzoic acids.

2 : 2-*Dichlorodiazoaminobenzene*, $C_6H_4Cl\cdot N_2\cdot NH\cdot C_6H_4Cl$, crystallises in golden-yellow crystals, softens at 80°, and melts at 90°. o-*Diazoaminobenzoic acid*, $CO_2H\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4\cdot CO_2H$, forms brownish-yellow plates and melts at 123°. m-*Tolueneazo-β-naphthol*,

$$C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot OH,$$

crystallises in pale red needles, melts at 141°, and is very slightly soluble in alkalis. as-m-*Xyleneazo-β-naphthol*, $C_6H_3Me_2\cdot N_2\cdot C_{10}H_6\cdot OH$, forms red needles, melts at 166°, and is soluble in alcohol or ether, but insoluble in water, alkalis, or dilute acids. *a-Naphthaleneazo-β-naphthol*, $C_{10}H_7\cdot N_2\cdot C_{10}H_6\cdot OH$, crystallises in violet-red columns, melts at 228—229°, and is very sparingly soluble in alcohol and insoluble in water, alkalis, or dilute acids. o-*Chlorobenzeneazo-β-naphthol*,

$$C_6H_4Cl\cdot N_2\cdot C_{10}H_6\cdot OH,$$

forms red prisms, melts at 163°, and is insoluble in water, alkalis, or dilute acids. m-*Chlorobenzeneazo-β-naphthol* forms red leaflets and melts at 158°. o-*Hydroxybenzeneazo-β-naphthol*,

$$OH\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH,$$

crystallises from ethyl acetate in dark violet crystals, melts at 193°, and is soluble in dilute solutions of alkali hydroxides. p-*Hydroxybenzeneazo-β-naphthol* forms red crystals, melts at 194° and resembles the preceding compound in regard to solubility. *β-Naphthol*-o-*azobenzoic acid*, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot CO_2H$, forms brick-red needles, melts at 268°, and is soluble in alcohol, but only slightly so in alkalis. *β-Naphthol*-m-*azobenzoic acid* separates in pale red needles, melts at 243°, and is very similar to the ortho-compound. *β-Naphthol*-p-*azobenzoic acid* crystallises in red needles, melts and decomposes at 301°, and is very sparingly soluble in most organic solvents, but more so in alkali hydroxides. *β-Naphthol*-m-*azobenzonitrile*,

$$OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot CN,$$

forms small, orange-red crystals, melts at 186°, and is very readily soluble in acetone and somewhat less so in alcohol or ether. *β-Naphthol*-

p-*azobenzonitrile* crystallises in small, blood-red prisms, melts at 236°, and is sparingly soluble in organic solvents. 4-*Amino*-2 : 3′-*dichloroazobenzene*, $C_6H_4Cl\cdot N_2\cdot C_6H_3Cl\cdot NH_2$, crystallises in golden-yellow needles and melts at 127°; the *hydrochloride*, $C_{12}H_9N_3Cl_2,HCl$, crystallises in small, violet crystals. 4-*Acetylamino*-2 : 3′-*dichloroazobenzene*, $C_6H_4Cl\cdot N_2\cdot C_6H_3Cl\cdot NHAc$, separates from dilute alcohol as a yellowish-brown, crystalline mass, melts at about 165°, and is insoluble in water. 2 : 3′-*Dichloroazobenzene*-4-*azo*-β-*naphthol*,

$$C_6H_4Cl\cdot N_2\cdot C_6H_3Cl\cdot N_2\cdot C_{10}H_6\cdot OH,$$

forms scarlet-red, microscopic crystals, melts at 226°, and is very sparingly soluble in organic solvents with the exception of glacial acetic acid and toluene. 4-*Amino*-3 : 2′-*dichloroazobenzene*,

$$C_6H_4Cl\cdot N_2\cdot C_6H_3Cl\cdot NH_2\ (?),$$

crystallises in yellow needles, melts at 113°, and combines with β-naphthol to form a dark red *diazo-compound* which melts at 226°.

The preceding substances are soluble in organic solvents except where otherwise stated.

The last-named compound, of which only a small quantity was obtained, may possibly be identical with 4-amino-2 : 3′-dichloroazobenzene. Whilst 3 : 3′-dichlorodiazoaminobenzene reacts readily with *m*-chloroaniline hydrochloride to form 4-amino-2 : 3′-dichloroazobenzene, 2 : 2′-dichlorodiazoaminobenzene gives only 2 per cent. of the theoretical yield of an isomeric dichloroaminoazo-compound, and thus, in this particular, closely resembles the 4 : 4′-derivative, which is incapable of reacting with *m*-chloroaniline hydrochloride. E. W. W.

Indulines of the Aminoazobenzene Fusion. OTTO FISCHER and EDUARD HEPP (*Zeit. Farb. Text. Chem.*, 1902, i, 457—459).—The following substances have hitherto been isolated from the aminoazobenzene fusion: azophenine, anilinophenosafranine, anilinomauveine, phenylanilinomauveine, *p*-phenylenediamine, di-*p*-aminodiphenylamine, and a small amount of diphenylfluorindene. Anilinophenosafranine, when treated with excess of mineral acids, yields a mixture of normal and acid salts which are not readily separated by crystallisation; pure specimens of the normal salts are most conveniently obtained by the use of the calculated quantities of the acids. When diazotised, this base gives rise to anilinoaposafranine, $C_{24}H_{18}N_4$.

The blue induline colouring matters are probably *p*-quinone derivatives, and it is quite likely that certain safranine derivatives are also capable of behaving, not only as *o*-quinone compounds, but also as derivatives of *p*-quinone. This view is supported by the fact that several safranine derivatives have been found to give oximes; aposafranine, for example, condenses with hydroxylamine when this reagent is present in excess. G. T. M.

Dynamical Experiments on the Formation of Azo-dyes. V. HEINRICH GOLDSCHMIDT and HANS KELLER (*Ber.*, 1902, **35**, 3534—3549. Compare Abstr., 1897, i, 279; 1898, ii, 20; 1899, ii, 276; and 1900, i, 367).—This part of the work is an examination of the influence of substituents on the rate of coupling of various tertiary amines with *m*- and *p*-diazobenzenesulphonic acids. The amines used

were dimethyl-and dipropyl-anilines, dimethyl- and diethyl-*m*-toluidines, and dimethyl- and diethyl-*m*-chloroanilines.

Dipropylaniline, obtained by heating aniline hydrobromide with propyl alcohol for eight hours in a sealed tube at 145—150°, boils at 238°. *Dipropylaminoazobenzene*-p-*sulphonic acid* crystallises with H_2O in red, microscopic, six-sided plates, and forms a crystalline, monohydrated *barium* salt. *Dimethyl*-m-*chloroaminoazobenzene*-p-*sulphonic acid* crystallises from water in small, ruby-red needles, decomposes when heated, and forms a yellow, crystalline *barium* salt with $3H_2O$. *Diethyl*-m-*chloroaminoazobenzene*-p-*sulphonic acid* crystallises with $2H_2O$ in ruby-red needles, and forms easily soluble alkali salts and a *barium* salt, with $1\frac{1}{2}H_2O$, which crystallises in long, yellow needles. The majority of these tertiary bases are so weak that they require more than the equivalent quantity of dilute hydrochloric acid for solution. The methods employed were exactly similar to those previously described (*loc. cit.*). Comparisons of the velocity of formation of the azo-compounds between dimethyl-, diethyl-, and dipropyl-aniline show that the replacement of methyl by ethyl lowers, and that of ethyl by propyl increases, the velocity. The *m*-toluidine bases couple very rapidly and the bases containing chlorine more slowly than the corresponding unsubstituted compounds. The paper also includes a discussion of the hydrolytic constants of the various tertiary amines used. R. H. P.

The Iodation of Proteids. II. C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1902, 36, 343—390. Compare Abstr., 1902, i, 251 and 732; ii, 627).—The following products, namely, hydrogen iodide, iodoform, carbon dioxide, formic and acetic acids, ammonium iodide and iodate, and probably *p*-iodocatechol, have been proved to be formed during the iodation of coagulated and non-coagulated albumin, albumin from yolk of egg, vitellin, and casein.

These compounds are regarded as being produced by the action of iodine on tyrosine obtained by the decomposition of the proteid, and the relative amounts of certain of the products support this conclusion.

In each case, the amounts of hydrogen iodide produced at 100° and at blood heat were determined. The amounts of some of the other products formed have also been determined.

The estimation of the iodoform was effected by (*a*) titration with $N/20$ thiosulphate for the free iodine, (*b*) titration with $N/10$ silver nitrate to give the total free iodine and iodine as iodide, (*c*) titration with $N/10$ silver nitrate after reduction with zinc dust free from chloride to give the total iodine (free $+ HI + CHI_3$).

For the detection of acetic and formic acids, the mixture was shaken with mercury to remove iodine and iodoform, the iodide then oxidised with very dilute iodic acid solution and hydrochloric acid, and the iodine removed by mercury, the solution finally being neutralised with sodium carbonate and evaporated. J. J. S.

The "Gold Number" of Proteids. FRIEDRICH N. SCHULZ and RICHARD ZSIGMONDY (*Beitr. chem. Physiol. Path.*, 1902, 3, 137—160). —The capacity of colloidal solutions to protect a colloidal solution of

gold against the precipitating action of an estimated quantity of sodium chloride is expressed as the gold number, this being defined precisely as the number of milligrams of colloidal solution which protects 10 c.c. of gold solution against the action of a 10 per cent. solution of sodium chloride. The present experiments relate to the gold numbers of the proteid of egg-white; these are globulin, 0·02 to 0·05; ovomucoid, 0·04 to 0·08; crystallised albumin, 2 to 8; a mixture of ovomucoid and amorphous albumin, 0·03 to 0·06; fresh white of egg, 0·08 to 0·15; albuminates, 0·01 to 0·04. The high number for crystalline egg-albumin is very noticeable; it is difficult to separate this substance from impurities, and the gold number affords a convenient means of gauging its purity. W. D. H.

The Precipitate Produced by adding Rennin to Solutions of Albumose. Maria Lawroff and Sergei Salaskin (*Zeit. physiol. Chem.*, 1902, **36**, 277—291).—All varieties of albumose in solutions of Witte's peptone are precipitated by the rennin action of gastric juice. There is, however, no ground for regarding this as evidence of the synthesis of more complex proteids, or 'regeneration of albumin.' The precipitate formed consists of substances with the character of albumoses. These substances are, however, not quite the same as Kühne's anti-albumid. They are digested by gastric juice and by intestinal juice; when subjected to pancreatic digestion, they yield leucine and tyrosine. The precipitates formed by the action of pancreatic and intestinal juices are very like anti-albumid. The name *plastein* is deprecated, and that of lab-albumose suggested. Pawloff's view that the peptic and rennin actions are due to the same ferment is supported. W. D. H.

Hydrolysis of Oxyhæmoglobin by the Aid of Hydrochloric Acid. Emil Fischer and Emil Abderhalden (*Zeit. physiol. Chem.*, 1902, **36**, 268—276. Compare Pröscher, Abstr., 1899, i, 653).—Crystallised oxyhæmoglobin obtained by Zinnoffsky's method (Abstr., 1886, 165) has been hydrolysed by concentrated hydrochloric acids and the resulting amino-acids separated by the distillation of their esters. By this means, alanine, 2·99; leucine, 20·88; aspartic acid, 3·43; glutamic acid, 1·11; phenylalanine, 3·53; and α-pyrrolidinecarboxylic acid, 1·52 per cent. (calculated on the globin), have been obtained in a pure form. The absence of glycine has also been demonstrated and Pröscher has already proved the presence of tyrosine. J. J. S.

Pectic Fermentation. Goyaud (*Compt. rend.*, 1902, **135**, 537—538).—The formation of pectic acid from pectin by the action of pectase is independent of the presence or absence of calcium salts. Gelatinisation takes place even after all the calcium salts have been removed from the vegetable juice under examination, by precipitation with potassium oxalate. C. H. B.

Organic Chemistry.

Compounds of Aluminium Bromide with Bromine, Ethyl Bromide, and Carbon Disulphide. Wladimir A. Plotnikoff (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 697—706. Compare Abstr., 1899, i, 470; 1900, i, 323; 1901, ii, 316; 1902, ii, 21 and 639).—When dissolved in ethyl bromide, the compounds of the compositions $AlBr_3,Br_4,CS_2$ and $2AlBr_3,Br_4,CS_2$, previously described by the author (*loc. cit.*), give rise to a new *compound* of the formula $AlBr_3,Br_2,EtBr,CS_2$, which separates in pale yellow crystals melting at 69—71°. It is slowly decomposed by water according to the equation: $2(AlBr_3,Br_2,EtBr,CS_2) + aq. = 2AlBr_3, aq. + CBr_2(SEt)_2 + CS_2Br_4$. The *ethyl dibromodithiocarbonate* thus obtained in quantitative yield is deposited in orange-yellow crystals melting and decomposing at 68° and is soluble in ethyl bromide or alcohol and, to a slight extent, in ether; with dilute aqueous ammonia, it yields *ethyl iminodithiocarbonate*, $NH{:}C(SEt)_2$, which separates from ether in thin, colourless, faintly-smelling needles melting at 33° and is soluble in light petroleum, alcohol, ethyl bromide, carbon disulphide, or ether. T. H. P.

Dinitroethanedinitronic Acid (*s*-Tetranitroethane). Roland Scholl and Albrecht Schmidt (*Ber.*, 1902, 35, 4288—4293. Compare Abstr., 1898, i, 345).—When treated with sulphuric acid, potassium dinitroethanedinitronate yields not the corresponding acid, but nitromethylenenitronic acid (dinitromethane), thus: $C_2(NO_2)_2({:}NO_2K)_2 + H_2O = NO_2{\cdot}CH{:}NO_2K + OH{\cdot}C(NO_2){:}NO_2H$. The other product of hydrolysis, dinitromethyl alcohol (or its decomposition products), has not been isolated.

Potassium nitromethylenenitronate is prepared by shaking potassium dinitroethanedinitronate with ether and dilute sulphuric acid and adding concentrated potassium hydroxide to the oil left on evaporating the ethereal layer; the salt crystallises in brownish-yellow, feathery crystals which explode at 218° (potassium dinitroethanedinitronate explodes at 275° and is pale yellow), and is identical with the salt prepared by reduction of potassium bromonitromethylenenitronate with potassium arsenite (Duden, Abstr., 1894, i, 101). When treated with bromine water, the salt gives an oil from which, by fractionation under reduced pressure, dibromodinitromethane can be isolated. The phenylhydrazine and benzylamine salts, which are both yellow, have been analysed.

The alcoholic mother liquors, obtained in the preparation of potassium dinitroethanedinitronate from potassium cyanide and bromopicrin, contain potassium bromonitromethylenenitronate and dibromodinitromethane. K. J. P. O.

Preparation and Properties of the Lower Chloromethyl Alkyl Ethers. Edgar Wedekind (*Chem. Centr.*, 1902, ii, 1301; from *Pharm. Zeit.*, 47, 836—837).—The lower chloromethyl alkyl ethers,

prepared as described in the German patent 135310, are very rapidly attacked by water, forming formaldehyde; the smaller the radicle contained in the alcohol which is simultaneously formed, the more rapidly is the ether decomposed. Polymeric formaldehyde is only obtained when the hydrolysis takes place very slowly and when the water present is insufficient for the complete decomposition. By the action of ammonia on chloromethyl methyl ether or on chloromethyl ethyl ether, hexamethylenetetramine is formed. By the action of lead formate and potassium acetate on chloromethyl methyl and ethyl ethers, the corresponding formates and acetates are obtained as colourless liquids which do not fume in the air, boil a little above 100°, and are decomposed by water, yielding formaldehyde, alcohol, and acid.

E. W. W.

Reduction of Acetol. André Kling (*Compt. rend.*, 1902, **135**, 970—972).—When acetol is oxidised in alkaline solution with cupric oxide, lactic acid is formed, and this seems to be incompatible with the constitution $CH_3 \cdot CO \cdot CH_2 \cdot OH$, usually accepted for acetol. The author endeavoured to find if acetol can react in tautomeric forms. Perkin showed that on reduction in aqueous solution with sodium amalgam, propylglycol is formed, and the reduction has now been more fully studied. When reduced, either when heated or in the cold, with sodium amalgam in alkaline solution, propylglycol and *iso*propyl alcohol are formed; with acid solutions in the cold, propylglycol and acetone are the products. Reduction with aluminium amalgam in neutral solution gives the same products as sodium amalgam in acid solution. These results indicate that in solution the acetol exists, at least partially, in another form besides $CH_3 \cdot CO \cdot CH_2 \cdot OH$, and the reduction is best explained by assuming the constitution $CH_3 \cdot C(OH) < \begin{smallmatrix} CH_2 \\ | \\ O \end{smallmatrix}$; this gives rise to $CH_3 \cdot CH(OH) \cdot CH_2 \cdot OH$ or to $CH_3 \cdot C(OH)_2 \cdot CH_3$, the latter then losing H_2O and yielding acetone or undergoing further reduction to *iso*propyl alcohol.

J. McC.

A Class of Double Salts. Daniel Strömholm (*J. pr. Chem.*, 1902, [ii], **66**, 423—474; 517—551. Compare Abstr., 1898, i, 624).—This paper deals with double salts of the types $RCl,HgCl_2$ to $RCl,6HgCl_2$, where RCl is a sulphine, thetine, or substituted ammonium chloride. When shaken with mercuric chloride solution, double salts of the intermediate types are differentiated into a salt containing less, and one containing more, mercuric chloride. The following *mercurichlorides* have not been previously described.

The methylethyl*iso*propylsulphine salt, $SMeEtPr^{\beta}Cl,6HgCl_2$, melts and decomposes at 208°. The methylethylbutylsulphine salt,

$$SMeEt(C_4H_9)Cl,6HgCl,$$

melts incompletely at 118°; that of methylethyl*sec.*butylsulphine, $SMeEt(C_4H_9)Cl,6HgCl_2$, melts and decomposes at 175—176°. The methyldipropylsulphine salt, $SMePr^{\alpha}_2Cl,2\frac{1}{2}HgCl_2$, crystallises in large, thin leaves and melts at 57°; that of methyldi*iso*propylsulphine, $SMePr^{\beta}_2Cl,HgCl_2$, forms small crystals.

The methylpropyl*iso*butylsulphine salt, $SMePr^{\alpha}(C_4H_9)Cl,6HgCl_2$,

melts incompletely at 118°; that of methyl*iso*propyl*iso*butylsulphine, $SMePr^{\beta}(C_4H_9)Cl,6HgCl_2$, has been analysed.

The methyldi*iso*butylsulphine salt, $SMe(C_4H_9)_2Cl,4HgCl_2$, melts incompletely at 103°. The salt $CH_2<\begin{matrix}CH(CO_2H)\\CH_2-CH_2\end{matrix}>SMeCl,6HgCl_2$ crystallises in small rhombohedra.

The methylammonium chloride salt has the composition

$$NH_3MeCl,2HgCl_2;$$

a salt with a larger proportion of mercuric chloride does not seem to be formed.

The dimethylammonium salt, $NH_2Me_2Cl,3HgCl_2,H_2O$, does not conform to the type $2RCl,5HgCl_2$ (Topsöe).

The *mercurichlorides* of trimethylammonium, $NHMe_3Cl,6HgCl_2,H_2O$, tetramethylammonium, $NMe_4Cl,6HgCl_2$, diethylammonium, $NH_2Et_2Cl,6HgCl_2,H_2O$, triethylammonium, $NHEt_3Cl,6HgCl_2$, tetraethylammonium, $NEt_4Cl,6HgCl_2$, phenyltrimethylammonium, $NMe_3PhCl,6HgCl_2$, and phenylethyl*iso*propylammonium,

$$NHEtPr^{\beta}PhCl,4HgCl_2,$$

were prepared; the last named crystallises in needles and melts at 137—140°.

Trimethylenehexamethyldiammonium mercurichloride,

$$C_3H_6(NMe_3)_2Cl_2,6HgCl_2,$$

when shaken with ether, is decomposed into mercuric chloride and $C_3H_6(NMe_3)_2Cl_2,2HgCl_2$.

Tetramethylpiperazinium di-iodide, $C_4H_8(NMe_2)_2I_2$, formed by the action of methyl iodide and sodium hydroxide on piperazine, is an insoluble, crystalline salt. The *mercurichlorides*, $C_8H_{20}N_2Cl_2,4HgCl_2$ and $C_8H_{20}N_2Cl_2,6HgCl_2$ ($7HgCl_2$?), have been analysed.

Hübner and Athenstädt's ethylenediphenyltetramethyldiammonium chloride (Abstr., 1884, 1317) is phenyltrimethylammonium chloride as it forms a *mercurichloride*, $NPhMe_3Cl,6HgCl_2$.

The paper contains a discussion of the relation between the physical properties of the *mercurichlorides* containing the largest proportion of mercuric chloride and the structure of these double salts and of the bases from which they are derived. G. Y.

Preparation of Unsaturated Aliphatic Acids with a Double-linking in the $\alpha\beta$-Position. HANS RUPE, MAX RONUS, and WALTHER LOTZ (*Ber.*, 1902, 35, 4265—4272).—With the object of preparing $\alpha\beta$-unsaturated fatty acids, the authors have used the method recommended by Crossley and Le Sueur (Trans., 1899, 75, 161, and 1900, 77, 83), which consists in heating the esters of the α-bromo-fatty acids with a tertiary amine such as quinoline or diethylaniline. It is found, however, that not only the $\alpha\beta$-, but also the $\beta\gamma$-unsaturated acids are formed under these conditions, the proportion of the latter increasing with the increase in the molecular weight of the acid. When ethyl α-bromovalerate (1 mol.) was heated with quinoline (2 mols.), a vigorous reaction set in at 160°; from the hydrolysed product of the reaction, the $\beta\gamma$-unsaturated acid was separated, by conversion into the lactone, by means of sulphuric acid, according to Fittig's method. $\Delta^{\alpha\beta}$-*Heptenoic acid*, $CH_2Me\cdot[CH_2]_2\cdot CH:CH\cdot CO_2H$,

is formed together with the isomeric $\beta\gamma$-unsaturated acid when ethyl α-bromoheptoate is heated with quinoline; the mixture of acids obtained on hydrolysis must be treated four times with sulphuric acid in order to convert the whole of the $\beta\gamma$-unsaturated acid into the lactone: the heptenoic acid thus obtained is a colourless oil boiling at 225—228° under 737 mm., and at 120—122° under 11·5 mm. pressure, and does not solidify at $-17°$; it has a sp. gr. 0·9575 at 20°, n_D 1·4488, and K 0·0015; on oxidation with permanganate, only valeric acid is formed, whereas if any of the $\beta\gamma$-unsaturated acid is present, butyric acid is also produced. The *calcium* salt of $\Delta^{\alpha\beta}$-heptenoic acid forms readily soluble needles; the *silver* salt was obtained as an amorphous powder, the *copper* salt in bluish-green, and the *cadmium* salt in colourless leaflets.

γ-Heptolactone, $\underbrace{CH_2Me \cdot CH_2 \cdot CH \cdot [CH_2]_2 \cdot CO}_{O}$, is a mobile oil with a powerful odour, boiling at 111° under 11 mm. pressure; it yields the *barium* salt of γ-hydroxyheptoic acid, which forms a white, amorphous powder. K. J. P. O.

Mixed Glycerides in Olive Oils. III. David Holde (*Ber.*, 1902, 35, 4306—4310. Compare Holde and Stange, Abstr., 1901, i, 577).—The oleodimargarine previously isolated gives, with Hübl's reagent in chloroform solution, a *chloroiodide*,

$$C_3H_5(C_{17}H_{33}O_2)_2 \cdot C_{18}H_{33}O_2ClI,$$

which, after being purified by solution in ether and precipitation with alcohol at $-20°$, melts at 24—25°.

Solid oleodimargarine only forms a very small proportion (1·5 per cent.) of most olive oils, and they also contain mere traces of triglycerides of fatty acids; the fatty acids which are found in these oils are apparently present as glycerides containing 1 mol. of glycerol combined with 1 mol. of saturated fatty acid and 2 mols. of oleic acid. When the ethereal mother liquors from the oleodimargarine are cooled to $-50°$ to $-60°$, a gelatinous mixture separates which contains 15·6 per cent. of fatty acids, probably combined as just indicated; after purification from oleodimargarine, the iodine number points to a composition approximating to that of margarodiolein or palmitodiolein. This product failed to give a solid chloroiodide.

Ethyl margarate, prepared by ethylating margaric acid, obtained by Krafft's method, melts at 24—25°; the isomeric ethyl daturate melts at 27°, whilst the ethyl salt, prepared from the margaric acid obtained from the oleodimargarine of olive oil, apparently consists of a mixture of two substances melting at 24° and 30° respectively, which can be separated by fractional crystallisation.

It has been stated by Henriques that a source of error in determining the molecular weight of a fatty acid lies in the acid becoming slightly esterified during crystallisation from alcohol; the author's experiments with palmitic acid do not support this view, as the acid remains quite unchanged when heated with alcohol. W. A. D.

Datura Oil. David Holde (*Chem. Centr.*, 1902, ii, 1417—1418; from *Mitt. Techn. Vers.-A., Berlin*, 20, 66—67).—The greenish- to

brownish-yellow oil extracted from the air-dried seeds of *Datura Strammonium* by means of benzene (yield, 16·7 per cent.) has a characteristic odour, a sp. gr. 0·9175 at 15°, an iodine number 113, and a saponification number 186. It begins to gelatinise at 0°, forms a thin paste when quickly cooled at −5°, becomes rather viscous at −15°, and at 20° flows from an Engler's apparatus at 1/9th the speed of water. Since the oil, on exposure to air, forms thick, resinous layers and, when heated in thin layers at 50°, rapidly dries to a solid mass, it probably either contains glycerides of very unsaturated acids or, like wood oil, undergoes intermolecular change. In addition to Gérard's daturic acid (*Compt. rend.*, 1890, **110**, 305, 565, and Abstr., 1892, 582), two more acids have been isolated from the solid acids of the oil by repeated fractionation by means of magnesium acetate. One of these acids has a molecular weight of 261 and melts at 60—62°, whilst the other has a molecular weight greater than 286 and melts at 53—54°. E. W. W.

Action of Mixed Organomagnesium Compounds on the Esters of Ketonic Acids. Victor Grignard (*Ann. Chim. Phys.*, 1902, [vii], **27**, 548—574. Compare Abstr., 1902, i, 420, and this vol., i, 31).—This paper is a more detailed description of work previously published, and contains the following additional facts.

Methyl α-ethylbutyrate has a sp. gr. 0·8886 at 12·5°/4° and n_D 1·40669. The *semicarbazone* of methyl *iso*butyl ketone crystallises in leaflets melting and decomposing at 132—133°. On adding methyl magnesium iodide to ethyl ethylideneacetoacetate, instead of methyl *iso*butyl ketone, a *polymeride* is formed which boils at 200° under 10 mm. pressure.

Methyl diethylacetoacetate is readily prepared by the prolonged action of ethyl iodide and sodium methoxide on ethyl acetoacetate and boils at 206—207° under 750 mm. pressure.

Ethyl phenylmethylglycollate boils at 129—130° under 13 mm. pressure, and ethyl phenylethylglycollate at 143° under 20 mm. pressure. The glycol obtained from ethyl lævulate and *iso*amyl magnesium bromide, when heated with acetic anhydride, gives an oxide, $C_{20}H_{40}O$, which is a colourless liquid boiling at 175—178° under 20 mm. pressure. The oxide, $\begin{matrix}CH_2\cdot CMePh\\ | \\ CH_2 — CPh_2\end{matrix}\!\!>\!O$, crystallises in needles from methyl alcohol melting at 74°. K. J. P. O.

Synthesis of Ketones and Acylacetones from *C*-Acylacetic Esters. Louis Bouveault and A. Bongert (*Bull. Soc. chim.*, 1902, **27**, [iii], 1083—1088).—When acylacetic esters of the type $CRO\cdot CHAc\cdot CO_2R'$ are hydrolysed by hydrochloric acid or potassium hydroxide solutions, acetic acid, the ketone $COMe\cdot R$, carbon dioxide, and the alcohol $R'OH$ are produced. When hydrolysed by water in sealed tubes at 140—150°, the acylacetone $CH_2Ac\cdot CO\cdot R$, carbon dioxide, and the alcohol $R'OH$ result.

Methyl butyrylacetoacetate, $CPr^aO\cdot CHAc\cdot CO_2Me$, is hydrolysed by

solution of potassium hydroxide into methyl propyl ketone; the *semicarbazone* of this forms slender needles, melts at 112°, and is soluble in organic liquids and warm water. The ester, when hydrolysed by water, furnishes 70 per cent. of butyrylacetone.

The *sodium* derivative of butyrylacetone, obtained by the action of metallic sodium on the ketone dissolved in ether, forms white needles, melts at 152°, and is soluble in ether; small quantities of water transform it into a semi-transparent jelly.

Methylbutyrylacetone, $COMe \cdot CHMe \cdot COPr^{\alpha}$, produced by methylating the foregoing, is a colourless oil of pleasant odour; it boils at 80—90° under 20 mm. pressure, has a sp. gr. 0·955 at 0°/4°, and gives a violet-red coloration with ferric chloride; the *copper* derivative crystallises from mixtures of hot alcohol and chloroform in greyish-green needles and melts at 163°. The ketone is hydrolysed slowly by dilute alkali hydroxide solutions into acetic acid and ethyl propyl ketone.

*Methylpropyl*iso*oxazole*, $\begin{matrix} CH{:}CMe \\ | \\ CPr^{\alpha}{=}N \end{matrix}{>}O$ or $\begin{matrix} CH{:}CPr^{\alpha} \\ | \\ CMe{=}N \end{matrix}{>}O$, obtained by condensing butyrylacetone with hydroxylamine, is an oily liquid, has a pyridine-like odour, and boils at 75—76° under 20 mm. pressure.

Methylpropylpyrazole, either $\begin{matrix} CH{:}CPr^{\alpha} \\ | \\ CMe{=}N \end{matrix}{>}NH$ or $\begin{matrix} CH{:}CMe \\ | \\ CPr^{\alpha}{=}N \end{matrix}{>}NH$, or possibly a mixture of these two isomerides, produced by the action of hydrazine acetate on butyrylacetone, is a colourless, viscous liquid with a nauseating odour; it boils at 136—137° under 20 mm. pressure, and when treated with benzoyl chloride in the presence of pyridine furnishes *benzoylmethylpropylpyrazole*, a colourless liquid which can be distilled under reduced pressure. With semicarbazide, butyryl acetone gives *methylpropylpyrazolecarboxylamide*,

$$\begin{matrix} CH{:}CPr^{\alpha} \\ | \\ CMe{=}N \end{matrix}{>}N \cdot CO \cdot NH_2 \text{ or } \begin{matrix} CH{:}CMe \\ | \\ CPr^{\alpha}{=}N \end{matrix}{>}N \cdot CO \cdot NH_2,$$

which forms small, white crystals, melts at 95°, and is readily soluble in organic liquids with the exception of light petroleum.

iso*Valerylacetone*, $COMe \cdot CH_2 \cdot CO \cdot C_4H_9$, a colourless liquid with a pleasant, fruity odour, boils at 76° under 19 mm. pressure, has a sp. gr. 0·936 at 0°/4°, and is coloured red by ferric chloride. The *copper* derivative forms pale blue crystals, melts at 142°, is slightly soluble in ether, but insoluble in light petroleum.

Hexoylacetone, $COMe \cdot CH_2 \cdot CO \cdot C_5H_{11}$, is a colourless liquid of pleasant, fruity odour; it boils at 100° under 20 mm. pressure, solidifies at −18°, and has a sp. gr. 0·936 at 0°/4°. The *copper* derivative forms pale blue crystals, melts at 136°, and is soluble in organic solvents. T. A. H.

Synthesis of Acylacetic Esters from *C*-Acylacetoacetic Esters. LOUIS BOUVEAULT and A. BONGERT (*Bull. Soc. chim.*, 1902, 27, [iii], 1088—1095. Compare preceding abstract).—*Methyl butyrylacetate*, $CPr^{\alpha}O \cdot CH_2 \cdot CO_2Me$, is formed when methyl butyrylacetoacetate (*C*-ester) is hydrolysed by dilute potassium hydroxide solution, sodium

methoxide, or dry gaseous ammonia; the first two reagents produce, in addition, methyl propyl ketone by secondary decomposition, and the last gives rise to acetamide. The ester is a colourless liquid of fruity odour; it boils at 86° under 14 mm. pressure, has a sp. gr. 1·037 at 0°/4°, is soluble in alkalis, and is coloured red by ferric chloride. The *copper* derivative forms green crystals, melts at 135°, and is soluble in organic liquids with the exception of light petroleum. The ethyl ester, produced in similar manner, has a sp. gr. 1·007 at 0°/4° (compare Blaise, Abstr., 1901, i, 363). Hydrazine hydrate reacts with these esters producing 3-*propylpyrazolone*, $\begin{array}{l} CH_2\text{—}CO \\ | \\ CPr^{\alpha}\text{=}N \end{array}\!\!>\!NH$; this forms rectangular crystals, melts at 198°, is soluble in alcohol, and insoluble in ether. The *sodium* derivative of methyl butyrylacetate in ethereal solution reacts with methyl chloroacetate on addition of alcohol to form *methyl butyrylsuccinate*, $CO_2Me\cdot CH(CPr^{\alpha}O)\cdot CH_2\cdot CO_2Me$, a colourless liquid, which boils at 153—154° under 25 mm. pressure, has a sp. gr. 1·125 at 0°/4°, and is hydrolysed by hydrochloric acid in closed tubes at 160—170° to methyl alcohol, carbon dioxide, and *butyrylpropionic acid*. The latter forms silky plates, melts at 46—47°, and is readily soluble in organic solvents.

*Methyl butyryl*iso*butyrylacetate* (*C*-ester), $CPr^{\alpha}O\cdot CH(CPr^{\beta}O)\cdot CO_2Me$, produced by the general method (this vol., i, 63) together with the isomeric *O*-ester, is a colourless liquid, which boils at 125° under 18 mm. pressure, has a sp. gr. 1·044 at 0°/4°, and is coloured red by ferric chloride. The *copper* derivative forms silky, blue needles, melts at 117·5°, and is soluble in organic solvents. With water at 100°, the ester furnishes *butyryl*iso*butyrylmethane*, $CPr_{\alpha}O\cdot CH_2\cdot CPr\ O$, a colourless liquid with an agreeable fruity odour, which boils at 89—90° under 20 mm. pressure, has a sp. gr. 0·9339 at 0°/4°, and is coloured red by ferric chloride. The *copper* derivative forms blue needles, melts at 123°, and dissolves in organic solvents.

*Methyl butyryl*iso*butyrylacetate* (*O*-ester) is a colourless liquid, boils at 128° under 18 mm. pressure, has a sp. gr. 1·029 at 0°/4°, and is not coloured by ferric chloride.

Ethyl iso*butyrylacetate*, $CPr^{\beta}O\cdot CH_2\cdot CO_2Et$, is a colourless liquid with a pleasant odour; it boils at 93—94° under 16 mm. pressure.

Methyl iso*valerylacetate*, $C_4H_9\cdot CO\cdot CH_2\cdot CO_2Me$, is a colourless liquid of pleasant odour; it boils at 95° under 15 mm. pressure and has a sp. gr. 1·006 at 0°/4°. The *copper* derivative forms small, green crystals, melts at 143°, and is soluble in organic solvents. With hydrazine hydrate, this ester furnishes 3-iso*butylpyrazolone*, which forms white leaflets melting and subliming at 239°, soluble in alcohol.

Methyl hexoylacetate, $C_5H_{11}\cdot CO\cdot CH_2\cdot CO_2Me$, boils at 118° under 19 mm. pressure, has a sp. gr. 0·9916 at 0°/4°, and solidifies when cooled; from it is obtained 3-*amylpyrazolone*, which forms white lamellæ melting at 195°.

Ethyl propionylacetoacetate (*C*-ester), when treated with gaseous ammonia, does not hydrolyse normally, but furnishes ethyl propionylacetate, ethyl acetoacetate, propionamide, and acetamide. T. A. H.

Reactions and Decompositions of *C*-Acyl Acetoacetates. LOUIS BOUVEAULT and A. BONGERT (*Bull. Soc. chim.*, 1902, [iii], 27, 1095—1100).—*Bisphenylpropylpyrazolone*,

$$\begin{array}{l}N{=}CPr^{\alpha}\\ |\\ NPh\cdot CO\end{array}\!\!>CH\cdot CH<\!\!\begin{array}{l}CPr^{\alpha}{:}N\\ \qquad\ \ |\\ CO{-}NPh\end{array},$$

formed when phenylhydrazine and methyl *C*-butyrylacetoacetate are mixed in the absence of a solvent, is a white, crystalline substance which melts at 346° and is oxidised by ferric chloride to a pyrazole-blue. When the two substances react in solution, there are produced acetylphenylhydrazine and 1-*phenyl*-3-*propylpyrazolone*,

$$NPh<\!\!\begin{array}{l}N{=}CPr^{\alpha}\\ \quad\ \ |\\ CO\cdot CH_2\end{array},$$

which forms rosettes of small, white needles, melts at 108—109°, and is soluble in chloroform, dilute acids, or alkalis, but less so in alcohol or ether.

3-*Propylpyrazolone*, produced together with acetylhydrazine when hydrazine hydrate reacts with the same ester dissolved in ether, separates from its solutions in boiling alcohol in colourless, rectangular crystals, melts at 198°, and is insoluble in ether and light petroleum.

Methyl 3-methyl-5-propylpyrazole-4-carboxylate,

$$NH<\!\!\begin{array}{l}N{=}CMe\\ \qquad\ |\\ CPr^{\alpha}{:}C\cdot CO_2Me\end{array},$$

produced by mixing solutions of the ester and hydrazine acetate in molecular proportion, is a viscous oil which boils at 179° under 10 mm. pressure; the *hydrochloride* is crystalline and is dissociated by water. The free *acid*, obtained by hydrolysing the methyl ester with dilute potassium hydroxide solution, forms white crystals, melts and decomposes at 228°, is soluble in alcohol, and insoluble in light petroleum. When heated at its melting point, the acid furnishes 3-methyl-5-propylpyrazole, identical with that obtained by the action of hydrazine on butyrylacetone (this vol., i, 142).

When methyl butyrylacetoacetate (1 part) is dissolved in sulphuric acid (2·5 parts) and the solution left for 15 days at the ordinary temperature, butyric acid and methyl acetoacetate are formed; by further action of sulphuric acid, the latter furnishes some *iso*dehydracetic acid; this decomposition is represented thus: $CPr^{\alpha}O\cdot CHAc\cdot CO_2Me \longrightarrow CPr^{\alpha}O\cdot O\cdot CMe{:}CH\cdot CO_2Me + H_2O \longrightarrow C_3H_7\cdot CO_2H + CH_2Ac\cdot CO_2Me$.

T. A. H.

Action of Acid Chlorides on the Sodium Derivatives of Substituted Acetoacetic Esters. LOUIS BOUVEAULT and A. BONGERT (*Bull. Soc. chim.*, 1902, [iii], 27, 1100—1106).—*Methyl α-butyrylpropionate*, $COPr^{\alpha}\cdot CHMe\cdot CO_2Me$, obtained by the action of methyl iodide and sodium methoxide on the sodium derivative of methyl butyrylacetoacetate, is a colourless liquid which boils at 89—90° under 16 mm. pressure and has a sp. gr. 1·005 at 0°/4°; it reacts with phenylhydrazine to form 1-*phenyl*-4-*methyl*-3-*propylpyrazolone*, $\begin{array}{l}CHMe\cdot CO\\ |\\ CPr^{\alpha}{=}N\end{array}\!\!>NPh$, which crystallises in small prisms, melts at 100°,

and is insoluble in petroleum. 4-*Methyl-3-propylpyrazolone*, obtained in similar manner by the action of hydrazine hydrate on the ester, forms small prisms, melts at 184°, and is slightly soluble in ether but insoluble in light petroleum.

Methyl methylbutyrylacetoacetates.—A mixture of the *O*- and *C*-esters is produced by the action of butyryl chloride on the sodium derivative of methyl methylacetoacetate. The product is a colourless liquid which boils at 122—130° under 20 mm. pressure; it neither forms a copper derivative, nor is it coloured by ferric chloride. Hydrazine acetate reacts with the mixture, forming, with the *O*-ester, butyrylhydrazine and dimethylpyrazolone, and with the *C*-ester, *methyl*-3 : 4-*dimethyl-5-propylpyrazole-4-carboxylate*, derived from a pyrazole of the formula $N{<}\begin{matrix}CH\cdot CH_2\\ \vert \\ N{=}CH\end{matrix}$, this is a colourless liquid with a peculiar odour; it boils at 156—158° under 14 mm. pressure and is converted by cold potassium hydroxide solution (20 per cent.) into the corresponding 3 : 4-dimethyl-5-propylpyrazole or an isomeride of this, a colourless liquid, which becomes yellow on standing and boils at 148—149° under 25 mm. pressure. With hydrazine hydrate, the *O*-ester furnishes the same products as with hydrazine acetate, whilst the *C*-ester is converted into 4-methyl-3-propylpyrazolone and acetylhydrazine. The mixed esters cannot be separated by heating with water in sealed tubes. T. A. H.

Mutual Isomeric Transformations of Acylacetoacetic Esters. Louis Bouveault and A. Bongert (*Bull. Soc. chim.*, 1902, [iii], 27, 1160—1164).—When methyl acetoacetate is treated with butyryl chloride in presence of pyridine (compare Claisen and Haase, Abstr., 1900, i, 373), 70 per cent. of the calculated yield of methyl *O*-butyrylacetoacetate is obtained; if diethylaniline be substituted for pyridine, the conversion is less complete: thus, by the action of *iso*valeryl chloride on methyl acetoacetate in presence of diethylaniline, only 55 per cent. of the theoretical yield of methyl *O*-*iso*valeryl acetoacetate is produced. When methyl *O*-butyrylacetoacetate in ethereal solution is treated with metallic sodium or potassium carbonate in presence of methyl acetoacetate, it is converted into the isomeric methyl *C*-butyrylacetoacetate to the extent of 25 and 35 per cent. respectively. This conversion of the enolic into the ketonic ester may also be brought about by the action of the sodium derivative of methyl acetoacetate; thus, methyl *O*-hexoylacetoacetate, when heated in ethereal solution with this reagent, furnishes 25 per cent. of the isomeric *C*-ester (compare Claisen and Haase, Abstr., 1901, i, 118). When ethyl *O*-acetylacetoacetate is heated at 200° for 7 hours, ethyl acetoacetate, ethyl acetate, acetic and dehydracetic acids are formed together with traces of acetylacetone; the latter is probably formed by the action of a small quantity of alkali dissolved out of the glass vessels employed; similarly, neither methyl *O*-hexoylacetoacetate nor methyl *O*-butyrylacetoacetate furnish the corresponding substituted acetones when heated at 200°. The authors are therefore unable to confirm the statement of Wislicenus and Körber (Abstr.,

1901, i, 187) that *O*-acylacetoacetates are converted into their ketonic isomerides by the action of heat. T. A. H.

Transformations of Salts of Pyruvic Acid. A. W. K. de Jong (*Rec. trav. chim.*, 1902, 21, 299—309. Compare Abstr., 1902, i, 72).—Barium pyruvate is converted into the parapyruvate (Wolff's salt, Abstr., 1899, i, 483) by solution in small quantities of boiling water, by evaporation or ebullition of its aqueous solutions, and by the action of condensing agents. There is also formed in these reactions some *barium metapyruvate*; this is a white, amorphous substance with a feebly alkaline reaction; it gives amorphous precipitates with lead and silver salts, is soluble in water when wet, but when dried on filter paper is converted into the gummy modification of barium pyruvate described by Berzelius. These condensed forms are reconverted into the simple pyruvate by warming their dilute aqueous solutions. *Lead pyruvate*, prepared by addition of a saturated solution of lead acetate to pyruvic acid, crystallises in needles.

The ammonium hydrogen sulphite *compound* of pyruvic acid and the corresponding *derivative* of ammonium pyruvate crystallise in needles, and when treated with phenylhydrazine yield the phenylhydrazone of pyruvic acid. T. A. H.

Action of Hydrogen Sulphide on Pyruvic Acid. A. W. K. de Jong (*Rec. trav. chim.*, 1902, 21, 295—298).—*a-Mercaptodilactic acid*, $S[CMe(OH)\cdot CO_2H]_2$, prepared by passing hydrogen sulphide through pyruvic acid, crystallises in colourless needles, melts at 94° with the evolution of hydrogen sulphide, and is resolved into its generators by water or alcohol. T. A. H.

Nomenclature of the Hydrogen Esters of Unsymmetrical Dibasic Acids. Rudolph Wegscheider (*Ber.*, 1902, 35, 4329—4330). —After considering the nomenclatures in use, the author advocates naming the ester acid with the smaller affinity constant the "a"-derivative, and its isomeride the "b"-derivative. W. A. D.

Thallium Oxalates. W. O. Rabe and Herm. Steinmetz (*Ber.*, 1902, 35, 4447—4453).—The preparation of the following *thallic oxalates* is described:—$TlH(C_2O_4)_2,3H_2O$, $TlH(C_2O_4)_2,4H_2O$, and $Tl_2H_4(C_2O_4)_5,6H_2O$. The first two are microcrystalline, and the last amorphous. When heated with an excess of oxalic acid, they yield the microcrystalline *thallous oxalate*, $Tl_2(C_2O_4)_2,3H_2O$. When the anhydrous oxalate, $TlH(C_2O_4)_2$, suspended in ether or alcohol, is treated with ammonia at 0°, the unstable *compound* $Tl(NH_4)(C_2O_4)_2,2NH_3$ is obtained, but at 45° the product formed is the *salt* $Tl(NH_4)(C_2O_4)_2$. The *pyridine* salt, $Tl(C_5NH_6)(C_2O_4)_2$, is obtained by analogous methods.

The double salt of pyridine oxalate and normal thallic oxalate, $Tl(C_5NH_6)_3(C_2O_4)_3$, crystallises from alcohol and ether in very slender leaflets which show double refraction; when treated with ammonia, it yields the *salt* $Tl(NH_4)_3(C_2O_4)_3$, which is decomposed by water.

R. H. P.

Microscopical Examination of [Succinates of] the Rare Earths. II. RICHARD J. MEYER (*Zeit. anorg. Chem.*, 1902, 33, 113—116. Compare this vol., i, 66).—The form assumed by cerium succinate depends on various circumstances; the occurrence of rhombic crystals must not be taken as indicating the presence of lanthanum. When the crystals are formed very slowly, these rhombs are alone produced, whilst starry aggregates are formed when crystallisation takes place more quickly.

It has further been proved that cerium and lanthanum succinates are isomorphous. A mixture of the two crystalline salts has exactly the appearance of pure cerium succinate, so that the presence of lanthanum could not be detected in this way. J. McC.

Preparation of Teraconic Acid. NIKOLAUS PETKOW (*Ber.*, 1902, 35, 4322—4324).—Details are given of a method for preparing teraconic acid in quantity by the sodium ethoxide condensation of ethyl succinate with acetone. W. A. D.

Camphoric Acid. XXII. Camphanic and Camphononic Acids. WILLIAM A. NOYES and ROBERT C. WARREN (*Amer. Chem. J.*, 1902, 28, 480—486).—When camphanic acid is heated with 10 per cent. sodium hydroxide for 24 hours on the water-bath, the sodium salt of *hydroxycamphoric acid* is produced; the *silver* salt was prepared and analysed. *Ethyl hydroxycamphorate* is a liquid of intensely bitter taste, has a sp. gr. of 1·0351 at 20°, and $[\alpha]_D$ 40° at 20°, and 39·6° at 28°; nitric acid converts it into the ester of camphanic acid, whilst Beckmann's mixture is without effect on it. i-*Camphanamide*, obtained by the action of ammonia on *i*-bromocamphoric anhydride, crystallises from alcohol in plates or prisms and melts at 196°. i-*Camphononic acid*, prepared by a modification of the method of Lapworth and Lenton (Trans., 1901, 79, 1283), melts at 232°; the *amide* melts at 215°. i-*Camphoric imide* crystallises from water in needles and melts at 249°. i-α-*Camphoramic acid* melts at 198°. The *chloride* of i-*aminolauronic acid* melts and decomposes at 266°; the *anhydride* of this acid melts at 203°. i-*Nitrosoaminolauronic anhydride* crystallises in lemon-yellow prisms and melts at 138°.

E. G.

Some Cases of the Wandering of Oxygen in the Molecule. II. Action of Ammonia on Alkyl-substituted Monobromosuccinic Acids. OSKAR LUTZ (*Ber.*, 1902, 35, 4369—4377. Compare Abstr., 1902, i, 596).—Citrabromomethylsuccinic acid (α-bromo-α-methylsuccinic acid), $CO_2H{\cdot}CH_2{\cdot}CMeBr{\cdot}CO_2H$, is converted by methyl-alcoholic ammonia into the *monoamide* of *α-hydroxy-α-methylsuccinic acid*, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CMe(OH){\cdot}CO_2H$, melting at 139—141°. When heated with dilute aqueous alkali hydroxides, *α-hydroxy-α-methylsuccinic acid* (citramalic acid) is produced. The β-bromo-α-ethylsuccinic acid of high melting point is converted under similar conditions into the *monoamide* of *β-hydroxy-α-ethylsuccinic acid*, $NH_2{\cdot}CO{\cdot}CHEt{\cdot}CH(OH){\cdot}CO_2H$, which crystallises in tabular aggregates melting at 158—159°. The free *acid* melts at 108—109° and

forms a crystalline *silver* salt. The β-bromo-α-ethylsuccinic acid of low melting point, on the other hand, when treated with a methyl-alcoholic solution of ammonia, yields the corresponding amino acid, *β amino-α-ethylsuccinic acid*, $CO_2H \cdot CHEt \cdot CH(NH_2) \cdot CO_2H$, which crystallises with $1H_2O$ in small needles and melts indefinitely at 110—112°, whilst the anhydrous acid melts at 132°. The *silver* salt crystallises in lustrous prisms. The acid has the normal molecular weight in aqueous solution, behaves as a monobasic acid, and has $K = 0.0343$. When heated at 100°, a new substance is formed which loses ammonia when boiled with aqueous baryta, but has not yet been further investigated. Finally, bromomethylsuccinic acid (itabromopyrotartaric acid) is converted by methyl-alcoholic ammonia into *β-itamalamic acid*, $NH_2 \cdot CO \cdot CH_2 \cdot CH(CH_2 \cdot OH) \cdot CO_2H$, the *ammonium* salt of which is very hygroscopic and melts at 98—101°. The *silver* salt is crystalline and yields the acid as a syrupy mass which gradually crystallises and melts indefinitely at 118—120°. When the ammonium salt is boiled with aqueous baryta, the whole of the nitrogen is evolved as ammonia, and paraconic acid is formed.

A. H.

Esters of Nitromalic and Nitrotartaric Acids. PAUL WALDEN (*Ber.*, 1902, **35**, 4362—4369. Compare Frankland, Heathcote, and Hartle, Trans., 1903, **83**, 154).—*Methyl nitromalate*,

$$CO_2Me \cdot CH_2 \cdot CH(O \cdot NO_2) \cdot CO_2Me,$$

is an oil having a sp. gr. 1·3184 at 20°, n_D 1·4390 at 13°, and $[\alpha]_D$ −33·01°; when cooled to −70°, it solidifies to a clear glass which slowly crystallises at 5—8°; the crystals melt at 24—25°. The ethyl ester (Henry, *Ber.*, 1870, **3**, 532) boils at 148—151° under 25 mm. pressure, has a sp. gr. 1·2090 at 20°, n_D 1·4325 at 13°, and $[\alpha]_D$ −31·24°; when cooled to −70°, the ester solidifies to a colourless glass, but does not crystallise. The n-*propyl* ester was not fully purified; it has a sp. gr. 1·1932 at 20°, n_D 1·4285 at 13°, and $[\alpha]_D$ −25·65°. The esters decompose very slowly on keeping, but do not racemise. The nitro-esters have a somewhat greater lævorotatory power than the acetates.

Methyl dinitrotartrate separates from ether in large crystals, melts at 92—94°, and has $[\alpha]_D$ +27·54° in alcohol. The ethyl ester (Henry, *loc. cit.*) crystallises in long needles, melts at 45—46°, and has $[\alpha]_D$ +29·87° in methyl alcohol. The *propyl* ester is an oil which has a sp. gr. 1·2088 at 20°, n_D 1·4330, and $[\alpha]_D$ +30·86°. The iso*butyl* ester was apparently not purified; it has a sp. gr. 1·1490 at 20° and $[\alpha]_D$ +32·89°.

T. M. L.

Inactivity of Mesotartaric Acid. LEON MARCHLEWSKI (*Ber.*, 1902, **35**, 4344—4345).—Mesotartaric acid, when partially dissociated, should yield an optically active ion, $CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CO_2$; but as equal numbers of dextro- and lævo-rotatory ions would be produced the aqueous solution would remain inactive. The inactivity would, however, be due to external, and not to internal, compensation.

T. M. L.

Methylene Compounds of Hydroxy-acids. Cornelis A. Lobry de Bruyn and William Alberda van Ekenstein (*Rec. trav. chim.*, 1902, **21**, 310—320. Compare Abstr., 1901, i, 120; 1902, i, 76 and 259).—In addition to the general reactions of these substances already described, it is now shown that they are decomposed by phenylhydrazine with the formation of the corresponding phenylacylhydrazines and formaldehydephenylhydrazone.

Monomethylene-d-*tartaric acid*, $CH_2<\begin{matrix}O\cdot CH\cdot CO_2H \\ O\cdot CH\cdot CO_2H\end{matrix}$, melts at 160°, has $[\alpha]_D$ −73°, and furnishes a *barium* salt crystallising in silky needles (compare Weber and Tollens, Abstr., 1898, i, 61); the corresponding *derivative* of *l*-tartaric acid has $[\alpha]_D$ +73°, but otherwise has the same properties as the foregoing.

Monomethylene-racemic and *-mesotartaric acids* melt respectively at 148° and 135°.

The *methylene* derivative of *malic acid* can be distilled under reduced pressure and has $[\alpha]_D$ −3°.

The *dimethylene* derivative of *saccharic acid* melts at 103°, has $[\alpha]_D$ +102°, and, like the trimethylene derivative, furnishes, on careful hydrolysis, the monomethylene saccharate of Henneberg and Tollens (Abstr., 1896, i, 645).

Methylene phenylglycollate, $\begin{matrix}CHPh\cdot O \\ CO——O\end{matrix}>CH_2$, is a neutral oil boiling at 157° under 27 mm. pressure and at 223° under atmospheric pressure; it has a sp. gr. 1·205 at 17·5°.

Methylene trichlorolactate is a neutral, crystalline substance, it melts at 32° and boils at 162° under 15 mm. pressure. *Trichlorolactylphenylhydrazine* melts at 180°.

Methylene α-hydroxybutyrate, $\begin{matrix}CH_2Me\cdot CH\cdot O \\ CO\cdot O\end{matrix}>CH_2$, is a liquid of pleasant odour which boils at 164° (compare Guye and Jordan, 1896, ii, 471); the corresponding *derivative* of β-hydroxybutyric acid, $\begin{matrix}CH_3\cdot CH\cdot CH_2\cdot CO \\ O—CH_2\cdot O\end{matrix}$, solidifies at 9°, boils at 190°, and has a sp. gr. 1·135 at 17°, whilst *methylene α-hydroxy*iso*butyrate*, $\begin{matrix}CMe_2—CO \\ O\cdot CH_2\cdot O\end{matrix}$, is a mobile liquid with a peppermint-like odour; it boils at 142° and has a sp. gr. 1·064 at 17°.

The *dimethylene* derivative of mucic acid melts at 160°, the *trimethylene* derivative, formed in small quantity with this, is an oil; either of these, when carefully hydrolysed, furnishes the *monomethylene* derivative, which crystallises with H_2O and then melts at 175°, but when anhydrous has the melting point 192°. The composition of these derivatives was ascertained by the method described by Weber and Tollens (*loc. cit.*). T. A. H.

The Nature of the Inactive Dimethylene Derivative of Racemic Acid. W. E. Ringer (*Rec. trav. chim.*, 1902, **21**, 374—375).—The melting point curve of mixtures of *d*-dimethylene tartrate and *i*-dimethylene racemate (de Bruyn and van Ekenstein, Abstr., 1901,

i, 120; 1902, i, 76) shows that the latter is a true racemic substance. The melting point of the racemate is scarcely affected by an admixture of small quantities (2·5 to 5 per cent.) of the *d*-compound. The eutectic mixture consists of 45 per cent. of the active and 55 per cent. of the inactive isomeride, and melts at 96°. T. A. H.

Electro-Synthesis in the Group of the Nitro-derivatives. C. Ulpiani and O. Gasparini (*Gazzetta*, 1902, **32**, ii, 235—242).—Whilst ethyl nitromalonate is not a conductor of electricity either in the free state or in aqueous alcoholic solution, the opposite is the case with its ammonium derivative. From this behaviour, it is concluded that ethyl nitromalonate is a true nitro-derivative of the constitution $CO_2Et{\cdot}CH(NO_2){\cdot}CO_2Et$, and that the ammonium compound has the *iso*nitro-structure, $C(CO_2Et)_2{:}NO{\cdot}ONH_4$. When, however, the latter is electrolysed in aqueous solution, it does not give rise to the free *iso*nitro-acid, but to *ethyl ethanedinitrotetracarboxylate*,

$$NO_2{\cdot}C(CO_2Et)_2{\cdot}C(CO_2Et)_2{\cdot}NO_2,$$

which separates from light petroleum in white crystals, melts at 65—66°, and is soluble in almost all organic solvents. This compound is evidently formed by the union of two anions of the ammonium derivative of ethyl nitromalonate, and the process represents a true electro-synthesis of a type different from those hitherto recorded. No answer has, however, been obtained to the question as to whether the ethyl nitroammoniomalonate has the *iso*nitro-structure given above or the enolic form proposed by Nef, $OEt{\cdot}C(ONH_4){:}C(NO_2){\cdot}CO_2Et$.

In the case of nitro-ammoniomalonamide, electrolysis of its aqueous solution does not lead to a similar synthesis, nitromalonamide being obtained.

With ammonium fulminurate, however, a condensation *product* is obtained crystallising in long, white needles which melt and decompose at 230°; this compound is being examined further.

T. H. P.

Oxidation of Alcohol and Aldehyde. Josef Slaboszewicz (*Zeit. physikal. Chem.*, 1902, **42**, 343—352).—Canizzaro's reaction, $2RCHO + H_2O = R{\cdot}CH_2{\cdot}OH + R{\cdot}CO{\cdot}OH$, is shown to take place even in neutral solution, and in the case of acetaldehyde the relation of the above change to the potential differences between platinum and aldehyde or alcohol has been investigated. By these electrical methods, it is shown that, in the oxidation of alcohol, not only aldehyde, but also higher oxidation products are obtained. J. C. P.

Solubility of Trioxymethylene in Solutions of Sodium Sulphite. Auguste Lumière, Louis Lumière, and Alphonse Seyewetz (*Bull. Soc. chim.*, 1902, iii, 27, 1212—1215).—The solubilities of trioxymethylene and sodium sulphite in water are increased in presence of each other, but the increase in either case is not directly proportional to the concentration of the solvent substance. The maximum solubility of trioxymethylene is 29 per cent. and is attained in presence of 45 per cent. of sodium sulphite, and, conversely, the maximum

solubility of the sulphite, namely, 55 per cent., is reached in presence of 25 per cent. of trioxymethylene; the latter, under these conditions, appears to undergo partial depolymerisation. The mixture in solution, when the maximum solubility of trioxymethylene is reached, corresponds with a substance of the formula $Na_2SO_3,2H{\cdot}CHO$, but no evidence of the existence of this could be found. T. A. H.

Methylglucoside and other Derivatives of Lactose. RUDOLF DITMAR (*Monatsh.*, 1902, 23, 865—876. Compare Bodart, Abstr., 1902, i, 347).—Hepta-acetylchlorolactose, when crystallised from a mixture of benzene and light petroleum, melts at 136—141°, but, when crystallised from ether, at 118—129°.

Hepta-acetylmethyllactoside, $C_{12}H_{14}O_4Me(OAc)_7$, formed when the chloro-compound is heated with silver carbonate in methyl alcohol solution, forms clusters of crystals, melts at 65—66°, has $[\alpha]_D$ $+6{\cdot}35°$ at 19°, is soluble in hot water, alcohol, or ether, reduces Fehling's solution, and, when treated with baryta, yields methyllactoside, or, on prolonged treatment, lactose. *Methyllactoside*, $C_{12}H_{21}O_{11}Me$, crystallises in needles, melts and decomposes at 170—171°, is easily soluble in water and acetic acid, insoluble in cold alcohol, reduces Fehling's solution only after prolonged heating, and is slightly hygroscopic.

When treated with acetic anhydride, saturated with hydrogen bromide, lactose yields *hepta-acetylbromolactose*, $C_{12}H_{14}O_3Br(OAc)_7$, which crystallises in long prisms, melts at 138° when crystallised from ether, or at 134° from a mixture of benzene and light petroleum, has $[\alpha]_D$ $+108{\cdot}17°$ at 14°, reduces Fehling's solution, and is soluble in alcohol, benzene, or acetone.

When heated with silver carbonate in methyl alcohol solution, hepta-acetylbromolactose yields a *hepta-acetylmethyllactoside*, which crystallises in needles, melts at 76—77°, has $[\alpha]_D$ $-5{\cdot}91°$ at 19°, and is isomeric with the acetylmethyllactoside obtained from the chloro-compound.

The action of silver acetate on hepta-acetylbromolactose, or of acetic anhydride and zinc chloride on lactose, leads to the formation of Schmöger's octo-acetyllactose (Abstr., 1892, 948). G. Y.

Relation of Hydriodic Acid and of its Salts to the Starch and Dextrin Iodides. F. E. HALE (*Amer. Chem. J.*, 1902, 28, 438—450).—Mylius (Abstr., 1887, 569) and Lonnes (Abstr., 1894, ii, 475) found that blue starch iodide contains hydriodic acid and iodine in the proportion of 1 : 4. A detailed account is given of experiments by means of which the author has confirmed this conclusion.

When the blue starch iodide is washed with a concentrated solution of potassium iodide, it is converted into a red compound in which the hydriodic acid and iodine are in the ratio of 1 : 2. The blue iodide of amidulin undergoes a similar change with solutions of potassium iodide of much less concentration than is required in the case of blue starch iodide. The colour of erythrodextrin red is changed by concentrated potassium iodide solution to orange-brown.

Mylius found a proportion of iodine in his starch iodide leading to

the formula $[(C_6H_{10}O_5)_4I]_4,HI$; Rouvier (Abstr., 1892, 1171) gave the formula $(C_6H_{10}O_5)_8I$, whilst in the present case (in which a rather viscous starch paste was employed) the starch iodide had the composition $[(C_6H_{10}O_5)_{16}I]_4,HI$.

It has been stated by Norris and Fay (Abstr., 1900, ii, 272) that the starch blue reaction is more delicate at low temperatures; the greater delicacy observed, however, was due to the influence of potassium iodide. It is found that the presence of 0·3 gram of potassium iodide in 300 c.c. of the liquid is sufficient to make the readings quite as sharp at the ordinary temperature as at 6°, whilst an excess of the salt over this amount fails to increase the delicacy of the reaction. E. G.

Hemicelluloses. Ernst Schulze and Nicola Castoro (*Zeit. physiol. Chem.*, 1902, 37, 40—53. Compare Abstr., 1893, ii, 139).—The cotyledons of the seeds of *Lupinus hirsutus*, when dried, ground, and successively extracted with ether, 0·1 per cent. aqueous sodium hydroxide, then with still more dilute alkali, water, and alcohol, leave a residue consisting to the extent of 90 per cent. of hemicelluloses, probably a paragalactoaraban or mixture of a galactan and araban.

Galactose and arabinose crystals have been actually isolated from the products obtained by hydrolysing the residue with 2 per cent. sulphuric acid. The arabinose was also confirmed by conversion into its phenylbenzylhydrazone melting at 172—174°.

The residue may also be hydrolysed when subjected to the action of 0·1 per cent. hydrochloric acid for 5—6 days at 40°, or by leaving in contact with the following enzymes: diastase, taka-diastase, ptyalin, or pancreatin. J. J. S.

Oxidation of Ethylamine. Eugen Bamberger (*Ber.*, 1902, 35, 4293—4299. Compare Abstr., 1901, i, 587).—When a solution of ethylamine is oxidised with monopersulphuric acid (Caro's acid), a series of substances is formed, the genetic relation of which is best shown by the following scheme: $CH_3{\cdot}CH_2{\cdot}NH_2 \rightarrow \{CH_3{\cdot}CH_2{\cdot}NH{\cdot}OH\} \rightarrow CH_3{\cdot}CH{:}NOH \rightarrow$ either $CH_3{\cdot}C(OH){:}NOH$, acetohydroxamic acid, or $\{CH_3{\cdot}CH{:}NO{\cdot}OH\} \rightarrow CH_3{\cdot}CH_2{\cdot}NO_2$. The acetaldoxime also breaks down into water and acetonitrile, the latter being partly converted into acetic acid. The formulæ enclosed in brackets represent the stages which have not been isolated. With other fatty amines, the hydroxylamine, the product of the first stage of the oxidation, has been isolated. The experiments were carried out with very concentrated aqueous solutions, or with liquid ethylamine, and with neutralised monopersulphuric acid free from hydrogen peroxide. From 3·7 to 3·8 grams of ethylamine, acetic acid, 2 grams; acetonitrile, 0·5 gram; acetaldoxime, 0·5 gram; nitroethane, 0·08 gram; acetohydroxamic acid, 0·01—0·02 gram were obtained. K. J. P. O.

Oxidation of Methylamine. Eugen Bamberger and Richard Seligman (*Ber.*, 1902, 35, 4299—4302. Compare preceding abstract).—The oxidation of methylamine by means of monopersulphuric acid is represented by the scheme: $CH_3{\cdot}NH_2 \rightarrow \{CH_3{\cdot}NH{\cdot}OH\} \rightarrow CH_2{:}NOH \rightarrow$ either $OH{\cdot}CH{:}NOH$, formohydroxamic acid, or

{CH_2:NO·OH}, methylenenitronic acid, ⟶ $CH_3\cdot NO_2$. The substances, the formulæ of which are enclosed in brackets, were not isolated. Formoxime, under the conditions of experiment, gives water and prussic acid, the latter yielding formic acid. The experiments were carried out in a manner very similar to that used in the case of ethylamine (*loc. cit.*). K. J. P. O.

Synthesis of Alkylated Pentamethylenediamine [αγ-Diaminopentane] and Alkylated Piperidines from β-Glycols. I. ADOLF FRANKE and MORIZ KOHN (*Monatsh.*, 1902, 23, 877—885. Compare this vol., i, 66).—Reduction of αγ-dicyanobutane with sodium and alcohol leads to the formation of αε-diamino-β-methylpentane and a small quantity of 3-methylpiperidine. *αε-Diamino-β-methylpentane*, $NH_2\cdot CH_2\cdot CHMe\cdot[CH_2]_3\cdot NH_2$, is a clear, colourless, mobile liquid, which boils at 78—80° under 13 mm. pressure, fumes slightly when exposed to the air, forms a cloud with hydrogen chloride, and is easily soluble in alcohol or water, but sparingly so in ether. The *hydrochloride* is hygroscopic and decomposes at 110°, or when kept in a vacuum over sulphuric acid or potassium hydroxide. The *platinichloride* forms a yellow, crystalline powder; the *aurichloride* forms brownish-yellow crystals and is easily soluble in water or alcohol. The *dibenzoyl* derivative crystallises in matted needles, sinters at 250°, and melts at 274°.

3-Methylpiperidine is formed when αε-diamino-β-methylpentane is distilled under the atmospheric pressure or when its hydrochloride is subjected to dry distillation. G. Y.

Alcohol Bases from Ethylenediamine: Ethylenebismorpholine. LUDWIG KNORR and HENRY W. BROWNSDON (*Ber.*, 1902, 35, 4470—4473).—Ethylenediamine (4 mols.) and ethylene oxide (1 mol.) slowly react in aqueous solution forming *ethanolethylenediamine*, $NH_2\cdot C_2H_4\cdot NH\cdot C_2H_4\cdot OH$, which is a colourless, deliquescent, oily liquid of ammoniacal odour, boiling at 238—240° under 752 mm. pressure; it absorbs carbon dioxide from the air and forms an easily soluble *platinichloride* which decomposes at 249°.

An excess of ethylene oxide slowly reacts with ethylenediamine hydrate forming *tetraethanolethylenediamine*, $C_2H_4[N(C_2H_4\cdot OH)_2]_2$; this resembles the monoethanol compound, but is very viscid and cannot be distilled. The *platinichloride* forms rhombic crystals which decompose at 196°.

Ethylenebismorpholine, $C_2H_4\left(N{<}^{C_2H_4}_{C_2H_4}{>}O\right)_2$, obtained when a mixture of ethylenediamine hydrate (1 mol.) and ethylene oxide (4 mols.) is heated with concentrated sulphuric acid in sealed tubes for 18 hours at 160—170°, separates from ether as an odourless, colourless, crystalline mass which melts at 74° and boils at 153—154° under 9 mm. pressure. The *dihydrochloride* crystallises in rhombic plates, the *platinichloride* in yellow prisms which melt and decompose at 257°, the *aurichloride* in bright yellow, rhombic needles which decompose at 197°, the *dipicrate* in yellow, rhombic plates which decompose at 230—236°, the *monopicrolonate* in golden-yellow needles

which decompose at 258°, and the *dimethiodide* in lustrous, rhombic plates which decompose at about 262°. The precipitates which the base gives with the various reagents for alkaloids are described.

R. H. P.

Morpholylhydrazine. LUDWIG KNORR and HENRY W. BROWNSDON (*Ber.*, 1902, **35**, 4474—4478).—*Diethanolhydrazine*, $NH_2 \cdot N(C_2H_4 \cdot OH)_2$, obtained from hydrazine hydrate and ethylene oxide, is a colourless oil which is not volatile with steam, and boils, decomposing to some extent, at 188—190° under 25 mm. pressure. It is not readily converted into morpholylhydrazine, since when heated with sulphuric acid much morpholine is formed.

Morpholylhydrazine, $O<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}>N \cdot NH_2$, best obtained by the reduction of nitrosomorpholine with zinc dust and dilute acetic acid, is a colourless, strongly refractive, hygroscopic oil with a characteristic odour. It boils at 168° under 767 mm. pressure, has a sp. gr. 1·0590 at 19·5°/4°, and n_D 1·4770 at 20°. The *hydrochloride* separates from alcohol in white, prismatic crystals and melts at 164°. The *benzoyl* derivative crystallises in lustrous plates melting at 214°, and the *benzylidene* compound in lustrous, rhombic plates melting at 89°. *Morpholylsemicarbazide* forms rhombic crystals which melt and decompose at 218°. *Methylmorpholylhydrazonium iodide*, from the hydrazine and methyl iodide, crystallises in lustrous plates and melts at 170—171°. *Dimorpholyltetrazone*, obtained by the oxidation of the hydrazine, crystallises from alcohol, melts at 152°, and decomposes when further heated.

R. H. P.

Double and Triple Thiocyanates. By HORACE L. WELLS (and, in part, with WILLIAM K. WALLBRIDGE, H. S. BRISTOL, C. S. LEAVENWORTH, R. T. ROBERTS, H. F. MERRIAM, and O. G. HUPFEL) (*Amer. Chem. J.*, 1902, **28**, 245—284).—Twenty-three double, and fourteen triple, thiocyanates are described. The type of the double thiocyanates corresponds in general with that of the double haloids; thiocyanates form double salts in smaller variety than do the haloids. With both haloids and thiocyanates, the valency of the negative metal has practically no influence on the type of double salt produced. *Ferric cæsium thiocyanate*, $Cs_3Fe(CNS)_6,2H_2O$, corresponding with the ferricyanides in type, crystallises only from very concentrated solutions. Of the *lead* salts prepared, $KPb(CNS)_3$, corresponds with the usual type of lead double haloids, whilst $K_6Pb(CNS)_8,2H_2O$ and $Cs_3Pb(CNS)_5$ represent new types. The *mercury* salts, $Cs_2Hg(CNS)_4,H_2O$, melting at 168—170°, and $CsHg(CNS)_3$ correspond with double haloids such as K_2HgCl_4,H_2O and $CsHgCl_3$. Cæsium mercuric thiocyanates of other types were not obtained. The manganous salt $Cs_4Mn(CNS)_6$ is analogous to the potassium manganothiocyanate described by Walden (Abstr., 1900, i, 430). The cuprous salt, $CsCu(CNS)_2$, was the only representative of this class of salt prepared by the author, who considers that Thurnauer's salt, 6KCNS,CuCNS (*Ber.*, 1890, **23**, 770), was a mixture. In this case, the thiocyanate affords a less variety of double salts than do the haloids, as three cæsium-cuprous chlorides are known. In con-

tradistinction to cuprous thiocyanate, silver thiocyanate readily forms double salts, for instance, $Cs_3Ag(CNS)_4$, $Cs_2Ag(CNS)_3$, $CsAg(CNS)_2$, $K_3Ag(CNS)_4$, $K_2Ag(CNS)_3$, $KAg(CNS)_2$, $MAg_2(CNS)_4,2H_2O$ (M = Ba, Sr, Ca). Magnesium cæsium thiocyanate, $Cs_2Mg(CNS)_4,2H_2O$, differs in type from known magnesium double haloids. The calcium and strontium cæsium thiocyanates, $Cs_2Ca(CNS)_4,3H_2O$ and

$$Cs_2Sr(CNS)_4,4H_2O,$$

are of particular interest, in so far that double haloids of the alkali metals with metals of the alkaline earths are unknown. There is also no double haloid corresponding with $CsTl_4(CNS)_5$. The triple salts, $Cs_3Ag_2Ba(CNS)_7$, $Cs_3Cu_2Ba(CNS)_7$, $Cs_3Ag_2Sr(CNS)_7$, and $Cs_3Cu_2Sr(CNS)_7$, are isomorphous, forming tetragonal pyramids resembling apophyllite. The calcium and magnesium triple salts are of similar type, namely, $Cs_2Ag_2M(CNS)_6,2H_2O$ (M = Ca, Mg, Mn). The following salts are also described: $Cs_2MNi(CNS)_5,2H_2O$ (M = Ag, Cu); $CsAgZn(CNS)_4,H_2O$; $Cs_2AgZn(CNS)_5$; $CsAg_3Zn_2(CNS)_8$; $CsAg_4Zn_2(CNS)_7$. The potassium silver barium salt,

$$K_4Ag_2Ba(CNS)_8,H_2O,$$

differs from its cæsium analogue in being crystallisable from water. The fourteen triple salts examined belong to seven distinct types, and they are regarded as molecular compounds of the same nature as double salts. A. McK.

Manganese Ferrocyanides. ALBERT E. DICKIE (*J. Amer. Chem. Soc.*, 1902, **24**, 1023—1024).—The following ratios of manganese to iron were found in the precipitates obtained as indicated:

	Ferrocyanide in excess.		Manganese in excess.	
	Mn.	Fe.	Mn.	Fe.
In neutral solution	103	: 100	107—108	: 100
In hydrochloric acid solution	106	: 100	107—110	: 100
In acetic acid solution...... ..	101—102	: 100	107	: 100

J. McC.

Compounds of Complex Cyanides with the Amines of the Fatty Series. PAUL CHRÉTIEN (*Compt. rend.*, 1902, **135**, 901—903). —Well characterised ferro- and ferri-cyanides of mono-, di-, or tri-*iso*amylamine are readily prepared by neutralising aqueous or alcoholic solutions of ferro- or ferri-cyanic acids with the corresponding quantity of the base. iso*Amylamine ferrocyanide*,

$$2C_5H_{11}\cdot NH_2,H_4Fe(CN)_6,H_2O,$$

forms large, pale yellow crystals which rapidly become green in contact with air; the *salt*, $4C_5H_{11}\cdot NH_2,H_4Fe(CN)_6$, forms white leaflets. iso*Amylamine ferricyanide*, $2C_5H_{11}\cdot NH_2,H_3Fe(CN)_6$, forms reddish-yellow crystals, and the *salt*, $3C_5H_{11}\cdot NH_2,H_3Fe(CN)_6$, yellow crystals. Di*iso*amylamine forms a *ferrocyanide*,

$$NH(C_5H_{11})_2,H_4Fe(CN)_6,$$

which crystallises in colourless cubes becoming green in the air; the other ferrocyanides could not be obtained. The *ferricyanide*,

$$3NH(C_5H_{11})_2,H_3Fe(CN)_6,$$

crystallises in yellow needles or thick prisms, and the *salt*,

$$2NH(C_5H_{11})_2,H_3Fe(CN)_6,$$

in yellow needles. The salts of tri-*iso*amylamine are the *ferrocyanide*, $N(C_5H_{11})_3,H_4Fe(CN)_6$, which forms white crystals becoming green in the air, and the *ferricyanides*, $3N(C_5H_{11})_3,H_3Fe(CN)_6$ and

$$N(C_5H_{11})_3,H_3Fe(CN)_6,H_2O,$$

both of which form yellow crystals. The acid ferricyanides of the di- and tri-*iso*amylamines easily decompose into the normal ferricyanides and the acid, whereas the acid ferrocyanides are stable.

K. J. P. O.

Action of Alkyl Haloids on Ammonium Dithiocarbamate. Marcel Delépine (*Compt. rend.*, 1902, **135**, 974—976. Compare Abstr., 1901, i, 518; 1902, i, 199, 353).—With ammonium dithiocarbamate, one mol. of the alkyl haloid gives alkyl dithiocarbamates (dithiourethanes) not substituted in the amino-group ($NH_2{\cdot}CS{\cdot}SNH_4 + RX = NH_2{\cdot}CS{\cdot}CR + NH_4X$), whilst two mols. give alkyl iminodithiocarbonates not substituted in the imino-group ($NH_2{\cdot}CS{\cdot}SR + R'X = NH{:}C(SR)(SR'),HX$). The following dithiourethanes have been prepared: $NH_2{\cdot}CS{\cdot}SMe$ melts at 40—42°; $NH_2{\cdot}CS{\cdot}SEt$ melts at 42°; $NH_2{\cdot}CS{\cdot}SPr^{\alpha}$ melts at 58°; $NH_2{\cdot}CS{\cdot}SPr^{\beta}$ melts at 97°; $NH_2{\cdot}CS{\cdot}SC_7H_7$ melts at 90°; and $NH_2{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2(p)$ melts at 135°. These are well-crystallised compounds which are insoluble in water, but easily soluble in ether, alcohol, benzene, or chloroform. When heated, they decompose, giving hydrogen sulphide, alkyl thiocyanates, carbon disulphide, and mercaptan. Acid anhydrides and chlorides give with them acyl derivatives identical with the compounds obtained by the action of thiolic acids on alkyl thiocyanates ($NH_2{\cdot}CS{\cdot}SR + (R'{\cdot}CO)_2O = R'{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}SR + R'{\cdot}CO_2H$), and these acyl derivatives do not combine with methyl iodide.

The alkyl iminodithiocarbonates are obtained by adding the alkyl iodide to a solution of the dithiourethanes in an indifferent solvent. The hydriodides of the following have been prepared: $NH{:}C(SMe)_2$, $NH{:}C(SEt)_2$, and $NH{:}C(SMe){\cdot}SBz$. They are colourless salts from which alkalis or ammonia separate colourless bases which are insoluble in water and have a disagreeable odour. These bases are very unstable and in this respect differ from the imino-substituted isomerides. When heated, they decompose, giving alkyl thiocyanate and mercaptan; the methylbenzyl derivative gives benzyl thiocyanate and not methyl thiocyanate. When aqueous solutions of the salts are heated, decomposition takes place, so that ammonium iodide and an alkyl dithiocarbonate are formed, $NH{:}C(SEt)_2,HI + H_2O = NH_4I + CO(SEt)_2$. Acetic acid decomposes the salts, giving an alkyl iodide (the alkyl being that of highest molecular weight) and an acyl-dithiourethane:

$$NH{:}C(SR)(SR'),HI + (CH_3{\cdot}CO)_2O = CH_3{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}SR + R'I + CH_3{\cdot}CO_2H.$$

Incidentally, this explains why alkyl iodides do not react on acyl-dithiourethanes. The secondary nature of these bases is proved by the fact that with nitrous acid they give a nitroso-compound having an intense blue colour, which is also imparted to any solvent in which the substance is dissolved.

J. McC.

α-Methylhydantoin. RUDOLF ANDREASCH (*Monatsh.*, 1902, **23** 803—815).—*Potassium uraminopropionate*, $C_4H_7O_3N_2K,H_2O$, formed by the action of potassium cyanate on alanine in aqueous solution (compare Urech, *Annalen*, 1873, **165**, 99), crystallises in delicate, silky needles, loses $1H_2O$ at 100°, and decomposes without melting at 200—205°. When evaporated with dilute hydrochloric acid, uraminopropionic acid is converted into α-methylhydantoin, which melts at 145° (compare Heintz, *Annalen*, 1873, **169**, 125, and Urech, *Ber.*, 1873, **6**, 1113). α-Methylhydantoin is also formed when alanine is heated with carbamide at 150—160°, and by the action of potassium cyanate on alanine ethyl ester hydrochloride, prepared by the action of hydrogen chloride on alanine in warm absolute alcoholic solution.

Potassium hydantoate, formed by the action of potassium cyanate on glycine in aqueous solution, crystallises in thick neeedles or prisms, melts and intumesces at 168°, and, when treated with dilute hydrochloric acid, yields hydantoin.

When heated with bromine in glacial acetic acid solution at 80—90°, α-methylhydantoin yields an unstable *bromo*-derivative, $C_4H_5O_2N_2Br$, and Grimaux's pyruvic ureide (*Ann. Chim. Phys.*, 1877, [v], **11**, 374), which becomes yellow at 240° and at 270° is converted into a brown, tarry mass. Bromo-α-methylhydantoin yields pyruvic ureide when boiled with water. G. Y.

Additive Compounds of *cyclo*Hexene. LÉON BRUNEL (*Compt. rend.*, 1902, **135**, 1055—1057).—When *cyclo*hexene, dissolved in ether or chloroform, is treated with iodine in presence of mercuric oxide and water, it yields *iodohydroxy*cyclo*hexane*, $C_6H_{10}I\cdot OH$, which forms large, colourless, rhombic prisms, is stable when exposed to light and air, melts at 41·5—42°, and sublimes in a vacuum at the ordinary temperature. It is insoluble in water, but soluble in most organic solvents, and volatilises in steam with partial decomposition.

If alcohol is used as the solvent in place of ether or chloroform, the *ethyl ether*, $C_6H_{10}I\cdot OEt$, is obtained as a colourless, oily liquid, which is not affected by light, boils at 118° under 47 mm. pressure, and has a sp. gr. 1·484 at 15°. The corresponding *methyl* compound boils at 114° under 49 mm. pressure and has a sp. gr. 1·565 at 14°. o-*Chloro-iodo*cyclo*hexane*, $C_6H_{10}ClI$, is obtained by using mercuric chloride in place of mercuric oxide in the above reaction; it is an almost colourless, oily liquid of camphoraceous odour, boils at 117—118° under 14 mm. pressure, has a sp. gr. 1·7608 at 14°, and volatilises readily, with slight decomposition, in water vapour. C. H. B.

Heptanaphthylenes. WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 720. Compare Abstr., 1902, i, 19).—A heptanaphthylene has been obtained with the specific rotation $[\alpha]_D + 108°54'$, which is the highest value yet observed for a heptanaphthylene.

T. H. P.

A New Method of Chlorinating Aromatic Hydrocarbons. ALPHONSE SEYEWETZ and BIOT (*Compt. rend.*, 1902, **135**, 1120—1122).—Plumbic ammonium chloride may be successfully employed for the

chlorination of aromatic hydrocarbons. Benzene and toluene require to be heated with the salt in sealed tubes, but with *p*-xylene, probably on account of the higher boiling point of this hydrocarbon, the mixture only requires to be boiled. Naphthalene and anthracene are chlorinated by heating the mixture at 150° and 200° respectively. The salt is prepared by passing chlorine into a suspension of lead chloride in hydrochloric acid until complete dissolution is effected; on addition of the calculated amount of ammonium chloride in water, the yellow double salt is precipitated. J. McC.

Action of Sulphur on Toluene and Xylene. LOUIS ARONSTEIN and A. S. VAN NIEROP (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 288—295).—Discrepancies in the molecular weights of sulphur obtained from the boiling points of solutions of sulphur in toluene and xylene suggested a possible chemical action. It was found that when sulphur was heated with toluene at 250—300° stilbene was formed, probably in accordance with the equation $2C_6H_5{\cdot}CH_3 + S_2 = C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5 + 2H_2S$. With *p*-xylene, the evolution of hydrogen sulphide is more rapid, and 4 : 4′-dimethylstilbene and 4 : 4′-dimethyldibenzyl are produced, the former being probably the primary product, which is then reduced to the latter by means of the hydrogen sulphide. The dimethyldibenzyl was obtained in two forms, (1) as a coarse, crystalline powder and (2) as thin leaflets with a silky lustre; both, however, gave the same melting point and solubility in alcohol. Analogous results were also obtained in the case of *m*-xylene. L. M. J.

Derivatives of 5-Chloro-1 : 2-dinitrobenzene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1902, 21, 320—326).—When methyl alcohol solutions of 5-chloro-1 : 2-dinitrobenzene (1 mol.) and sodium methoxide (1 mol.) are mixed, there is formed 5-chloro-2-nitrophenyl methyl ether. This reacts with sodium methoxide in methyl alcohol solution to form the mono- and di-methyl ethers of 2-nitroresorcinol, and when warmed with a mixture of nitric and sulphuric acids yields 5-*chloro*-2 : 4 : 6-*trinitrophenyl methyl ether*; which separates from alcohol in colourless crystals, melts at 88°, and, when treated with sodium methoxide in methyl alcohol, furnishes the corresponding dimethyl ether of trinitroresorcinol, whilst, with ammonia in alcohol, it yields 2 : 4 : 6-trinitro-*m*-phenylenediamine, with methylamine, the corresponding 2 : 4 : 6-trinitro-*m*-phenylenedimethyldiamine, and with aniline, 5-*anilino*-2 : 4 : 6-*trinitrophenyl methyl ether*. The latter occurs in yellow crystals, melts at 178°, and reacts with ammonia in alcohol, forming 1-*amino*-5-*anilino*-2 : 4 : 6-*trinitrobenzene*, and with methylamine to form 1-*methylamino*-5-*anilino*-2 : 4 : 6-*trinitrobenzene*; these are yellow, crystalline substances melting at 186° and 174° respectively.

5-*Chloro*-2-*nitrophenyl ethyl ether*, prepared by the same reaction as the methyl ether, melts at 63° and reacts in the same manner as its lower homologue; the following new derivatives have been prepared by the methods mentioned in the foregoing paragraph: 5-*chloro*-2 : 4 : 6-*trinitrophenyl ethyl ether* crystallises in colourless needles and melts at

51°. *Trinitro*-m-*phenylene*-s-*diethyldiamine* forms yellow crystals, melts at 144°, and is converted by nitric acid into *trinitro*-m-*phenylene*-s-*diethyldinitroamine*, a crystalline, yellow substance melting at 174°.

T. A. H.

Dibromodinitrobenzenes derived from *p*-Dibromobenzene. C. Loring Jackson and Daniel F. Calhane (*Amer. Chem. J.*, 1902, 28, 451—474).—The products of the nitration of *p*-dibromobenzene were first studied by Austen, who isolated two isomeric dibromodinitrobenzenes which he distinguished as α and β; he also found that the β-compound is 1 : 4-dibromo-2 : 6-dinitrobenzene. Calhane and Wheeler (Abstr., 1900, i, 146) have shown that the α-compound is 1 : 4-dibromo-2 : 3-dinitrobenzene. The third isomeride has now been isolated from the products of the reaction.

1 : 4-*Dibromo*-2 : 5-*dinitrobenzene* crystallises in long prisms of a yellowish-white colour, melts at 127°, and is soluble in benzene, chloroform, acetone, or carbon disulphide. On reduction, it is converted into 2 : 5-*dibromo*-p-*phenylenediamine*, which crystallises from chloroform in large, white plates of a pearly lustre and turns brown on exposure to light; it melts at 183—184° with formation of a dark blue substance, and is soluble in ether or acetone; the *hydrochloride* forms long, slender, white needles. When the diamine is oxidised with chromic acid, it is converted into 2 : 5-dibromo-*p*-quinone, which was first obtained by Sarauw (Abstr., 1881, 1136) by the action of ferric chloride on dibromoquinol.

When 1 : 4-dibromo-2 : 5-dinitrobenzene is heated with alcoholic ammonia at 100° in a sealed tube, 2 : 5-*dibromo*-4-*nitroaniline* is produced, which crystallises in deep brownish-yellow prisms, melts at 174—175°, and is soluble in benzene; its *hydrochloride* forms yellow needles. 4-*Bromo*-2 : 5-*dinitro*-1-*anilinobenzene*, $NHPh\cdot C_6H_2Br(NO_2)_2$, obtained by the action of aniline on 1 : 4-dibromo-2 : 5-dinitrobenzene, crystallises in orange-red, hexagonal prisms, melts at 153—154°, and is soluble in ether, benzene, chloroform, glacial acetic acid, or carbon disulphide.

When 1 : 4-dibromo-2 : 5-dinitrobenzene is treated with sodium ethoxide, 2 : 5-*dibromo*-4-*nitrophenetole* is produced, which crystallises from hot alcohol in needles or prisms, melts at 126°, and is soluble in benzene, chloroform, glacial acetic acid, or carbon disulphide. If the mixture of sodium ethoxide and dibromodinitrobenzene is heated, in addition to the dibromonitrophenetole, another substance is obtained which crystallises from dilute alcohol in yellowish-white needles, melts at 103—104°, is soluble in benzene, chloroform, or acetone, and is probably the *diethyl* ether of 4-bromo-6-nitroresorcinol; ethyl sodiomalonate reacts with this compound with the formation of a red *sodium* salt.

By the action of sodium ethoxide on 1 : 4-dibromo-2 : 3-dinitrobenzene, 2 : 5-*dibromo*-6-*nitrophenetole* is produced, which crystallises in transparent, lemon-yellow prisms, melts at 45°, and is readily soluble in the usual organic solvents; the yield is less than 18 per cent., sodium bromide and other substances being formed. If 1 : 4-dibromo-2 : 3-dinitrobenzene is boiled with solution of sodium hydroxide for

7—8 hours, 2 : 5-*dibromo-6-nitrophenol* is obtained, which crystallises in bright golden-yellow needles, melts at 77°, and is soluble in the usual organic solvents; its *barium* salt crystallises with $3H_2O$. E. G.

Derivatives of Phenylnitroethylene [β-Nitrostyrene]. JOHANNES THIELE and SIEGFRIED HAECKEL (*Annalen*, 1902, **325**, 1—18).—β-Nitrostyrene can be prepared in large quantities by condensing benzaldehyde with nitromethane in alcoholic solution in the presence of alkali; when the alkali is in the form of sodium methoxide, the *sodium* salt, $OH\cdot CHPh\cdot CH\colon NO\cdot ONa$, is obtained (Bouveault and Wahl, Abstr., 1902, i, 682). β-Bromo-β-nitrostyrene,

$$CHPh\colon CBr\cdot NO_2,$$

is prepared from the nitro-derivative by first forming the dibromo-additive product and then eliminating hydrogen bromide by means of sodium acetate (compare Priebs, Abstr., 1884, 313). The *potassium* salt of β-bromo-β-nitro-α-methoxyphenylethane,

$$OMe\cdot CHPh\cdot CBr\colon NO\cdot OK,$$

is obtained when the last-mentioned compound is suspended in methyl alcohol and treated with a methyl alcoholic solution of potassium hydroxide; it forms yellow leaflets and is converted by acids into the *ψ-acid*, $OMe\cdot CHPh\cdot CHBr\cdot NO_2$, which is a yellow oil with characteristic smell; it boils at 159° under 16 mm. pressure and solidifies in a freezing mixture. *ββ-Dibromo-β-nitro-α-methoxyphenylethane*,

$$OMe\cdot CHPh\cdot CBr_2\cdot NO_2,$$

prepared by treating the potassium salt just mentioned with bromine water, crystallises in white needles melting at 83° and is insoluble in alcoholic potash. The *dimethylacetal* of α-nitroacetophenone,

$$CPh(OMe)_2\cdot CH_2\cdot NO_2,$$

is obtained by boiling bromonitrostyrene with a large excess of methyl alcoholic potassium hydroxide; it crystallises in needles melting at 55·5—56° and is converted, by hydrolysis with concentrated hydrochloric or sulphuric acid in acetic acid solution, into α-nitroacetophenone (m. p. 105—105·5°).

β-*p*-Dinitrostyrene can be prepared in quantity by nitrating β-nitro styrene by a modification of Priebs' method (*loc. cit.*). From the *potassium* salt of β-*p*-dinitro-α-methoxyphenylethane,

$$NO_2\cdot C_6H_4\cdot CH(OMe)\cdot CBr\colon NO\cdot OK,$$

which is prepared by acting on β-*p*-dinitrobromostyrene with methyl alcoholic potash, the *ψ-acid* is obtained as white needles melting at 126·5—127°. From the potassium salt, a *dibromo*-derivative, $NO_2\cdot C_6H_4\cdot CH(OMe)\cdot CBr_2\cdot NO_2$, is formed by the action of bromine water; it crystallises in white needles melting at 160—160·5°. The *dimethylacetal*, $NO_2\cdot C_6H_4\cdot C(OMe)_2\cdot CHBr\cdot NO_2$, is obtained from the last-mentioned substance by treatment with excess of methyl alcoholic potash; it crystallises in white needles melting at 122·5—123°. The *dimethylacetal* of dinitroacetophenone is obtained from β-bromo-β-*p*-dinitrostyrene in a similar manner, and crystallises in white needles melting at 112·5°; it is soluble in alkalis, and is precipitated thence by bromine water as the monobromo-derivative just described. *α-p-Dinitroacetophenone*, $NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot NO_2$, is prepared from the dimethylacetal by cautious hydrolysis with hydrochloric acid; it forms

pale yellow plates melting at 148—148·5° and is decomposed by boiling with water into *p*-nitrobenzoic acid and nitromethane.

K. J. P. O.

Tetrahydronaphthalene contained in Coal-Tar. Johannes Boes (*Chem. Centr.*, 1902, ii, 1119; from *Ber. Deutsch. pharm. Ges.*, 12, 222—223).—By removing the homologues of coumarone and indene from the hydrocarbons contained in coal-tar and decomposing the sulphonic acids with steam, a product boiling at 204—205° is obtained; from this substance, tetrahydronaphthalene, apparently identical with that of Graebe and Bamberger (Abstr., 1884, 608), has been isolated. Tetrahydronaphthalene is at first colourless, but soon becomes yellow, is very readily attacked by sulphuric acid forming a sulphonic acid which is precipitated on the addition of water, and can be recrystallised from water. The sulphonic chloride is not easily prepared in a crystalline form; the sulphonamide crystallises from alcohol in long prisms and melts at 139°. Tetrahydronaphthalene is oxidised by dilute nitric acid or by an acid solution of potassium permanganate, yielding, in the former case, phthalic acid, and in the latter, *o*-carboxyphenylpropionic acid. E. W. W.

Constitution of Primary Dinitrohydrocarbons. Giacomo Ponzio (*J. pr. Chem.*, 1902, [ii], 66, 478—479. Compare Abstr., 1902, i, 334).—A reply to Scholl (Abstr., 1902, i, 753). G. Y.

Idryl (Fluoranthrene) and Fluorenonecarboxylic Acid. Guido Goldschmiedt (*Monatsh.*, 1902, 23, 886—896. Compare Abstr., 1878, 155; 1879, 167; 1881, 283).—Ethyl oxalate and benzaldehyde do not form condensation products with idryl.

The following derivatives of fluorenone-1-carboxylic acid have been prepared. The *chloride*, $CO{<}\begin{matrix}C_6H_3{\cdot}COCl \\ | \\ C_6H_4\end{matrix}$, formed by the action of thionyl chloride on the acid, crystallises from benzene in small, yellow needles and melts at 140°. The *ethyl ester*, formed from the chloride, crystallises in long, yellow, leaf-like needles and melts at 75—76°. The *amide* crystallises from alcohol in glistening, lemon-yellow needles and melts at 229—230°. The *oxime* crystallises in small prisms, melts and decomposes at 230°, and is easily soluble in cold aqueous alkalis or ammonia. The *phenylhydrazone* crystallises in glistening, lemon-yellow needles, melts and decomposes at 230—232°, is only slightly soluble in alcohol, benzene, or glacial acetic acid, but easily so in cold alkali carbonate solutions.

1-*Aminofluorenone*, $CO{<}\begin{matrix}C_6H_3{\cdot}NH_2 \\ | \\ C_6H_4\end{matrix}$, obtained from the amide of fluorenone-1-carboxylic acid by the action of bromine and potassium hydroxide, forms a yellow, crystalline powder, melts at 110°, is easily soluble in organic solvents, and moderately so in boiling water (compare Abstr., 1897, i, 68). The *hydrochloride*, $C_{13}H_9ON,HCl$, is hydrolysed by water; the *platinichloride*, $(C_{13}H_9ON)_2,H_2PtCl_6$, crystallises in dark yellow needles.

1-Hydroxyfluorenone, obtained by diazotisation of aminofluorenone, crystallises in intensely yellow needles, melts at 115°, dissolves in cold concentrated sulphuric acid with a wine-red colour, becomes orange-red in contact with potassium hydroxide solution, and is identical with the substance obtained by Staedel (Abstr., 1895, i, 147).

G. Y.

Acid Derivative of Ethyl Anilinomalonate. By RICHARD SYDNEY CURTISS (*Amer. Chem. J.*, 1902, **28**, 315—326).—The action of nitrous acid on ethyl anilinomalonate yields an oil having acid properties (compare Abstr., 1900, i, 482). A further study of this substance and, more particularly, determinations of its electrical conductivity have led the author to assign to it the constitution

$$\begin{matrix}OH\cdot N \\ PhN\end{matrix}\!\!>\!C(CO_2Et)_2$$

(ethyl α-phenylhydroxydiazomalonate) in preference to

$$NO\cdot NPh\cdot CH(CO_2Et)_2$$

(ethyl nitrosoanilinomalonate).

The oil is easily soluble in benzene, ether, alcohol, chloroform, or glacial acetic acid, and is readily decomposed by heat or by sunlight. Aqueous solutions of the sodium, potassium, and ammonium salts are unstable. When the oil is heated, nitrogen, nitric oxide, and carbon dioxide are evolved, and from the residue a crystalline substance melting at 111° is obtained. Reduction of the oil by zinc and acetic acid gives a product which melts at 44°, has strong reducing properties, and is oxidised to ethyl anilinomalonate by mercuric oxide.

A. McK.

Action of Succinic Acid on *p*-Anisidine. SAVERIO FICI (*Chem. Centr.*, 1902, ii, 1449; from *Boll. Chim. Farm.*, 41, 705—709. Compare Benevento, Abstr., 1899, i, 349; Piutti, Abstr., 1896, i, 223).—A better yield of Piutti's compound, melting at 243°, is obtained by heating a mixture of *p*-anisidine (2 mols.) and succinic acid (1 mol.) for four hours at 260° and thoroughly extracting the product with alcohol. The compound proved to be *di-p-methoxyphenylsuccinamide*, $C_2H_4\cdot(CO\cdot NH\cdot C_6H_4\cdot OMe)_2$; it crystallises in greyish-white crystals, is insoluble in alcohol, ether, light petroleum, benzene, or acetic acid, is not attacked by concentrated solutions of alkalis, and, on heating with concentrated hydrochloric acid for three hours at 130°, is decomposed, forming succinic acid and *p*-aminophenol hydrochloride. The *dinitro-derivative*, prepared by cautiously adding dimethoxyphenylsuccinamide to a cooled mixture of concentrated nitric and sulphuric acids, separates from acetic acid in golden-yellow crystals, melts at 215°, and is insoluble in water or ether. 3-*Nitro*-4-*aminophenol*, obtained by the action of concentrated hydrochloric acid on the dinitro-derivative at 130°, crystallises in dark red prisms and melts at 123°. E. W. W.

Influence of Substituents in the Nucleus on the Stability of Alkali Phenoxides towards Carbon Dioxide at the Ordinary Temperature. PAUL N. RAIKOW and IW. N. MOMTSCHILOW (*Chem. Zeit.*, 1902, **26**, 1237—1240).—The effect of passing carbon dioxide into solutions of the alkali salts of various phenols

has been studied in order to form an estimate of the influence exerted on the acidity of the phenols by the presence of various groups which replace hydrogen in the nucleus. All phenols having alkyl groups attached to the nucleus are readily precipitated. Phenol, the cresols, carvacrol, and thymol were investigated. The polyhydric phenols, resorcinol, quinol, pyrogallol, phloroglucinol, thioresorcinol, guaiacol, and *iso*eugenol were all immediately precipitated by carbon dioxide. Aminophenols are readily soluble in alkali hydroxides, but are again set free by carbon dioxide; *o*-, *m*-, and *p*-aminophenols, aminothiophenol, and diaminotetrahydroxybenzene were studied. The haloid derivatives of phenols, such as *s*-tribromophenol, *p*-iodophenol, and methyl di-iodosalicylate, are separated as easily from their alkaline solutions as the aminophenols. Salicylaldehyde, *p*-hydroxybenzaldehyde, and vanillin are only precipitated after long passage of carbon dioxide. The esters of hydroxy-acids, on the other hand, are just as readily precipitated as the cresols. The mononitrophenols are set free slowly from their alkaline solutions, but *s*-trinitrophenol, *s*-dinitroaminophenol (picramic acid), and nitrovanillin (2-methoxy-4-aldehydo-6-nitrophenol) cannot be precipitated by carbon dioxide from their alkaline solutions at the ordinary temperature and pressure. Of the naphthols, β-naphthol is thrown down more quickly than the α-derivative. 2 : 4-Dinitronaphthol cannot be precipitated. K. J. P. O.

Preparation of Tetrachlorophenol. ETIENNE BARRAL and E. GROSFILLEX (*Bull. Soc. chim.*, 1902, [iii], **27**, 1174—1178).—2 : 3 : 4 : 5-Tetrachlorophenol can be prepared either by passing into phenol, dry chlorine in sufficient quantity to form trichlorophenol, warming the latter at 80°, and then continuing the chlorination for 15 days, or by adding either 5 per cent. of antimony trichloride, 2—3 per cent. of iodine, or 5—6 per cent. of ferric chloride, when complete chlorination may be effected in a shorter time at the ordinary temperature. The crude product is washed with dilute acids and water, dried, and covered for 2 days with light petroleum; it is next dissolved in 5 per cent. solution of sodium hydroxide and treated with one-tenth of its weight of sodium peroxide; sufficient hydrochloric acid to precipitate 5—10 per cent. of the tetrachlorophenol is then added, and, from the filtrate, the remainder is precipitated in a pure state by the addition of excess of acid. The substance is purified by recrystallisation from light petroleum; it melts at 67·5° and can be slowly distilled under reduced pressure without decomposition (compare Zincke and Walbaum, Abstr., 1891, 708). T. A. H.

Derivatives of Phenyl Ether. IV. ALFRED N. COOK and GUY G. FRARY (*Amer. Chem. J.*, 1902, **28**, 486—490).—p-*Nitrophenyl* m-*tolyl ether*, $NO_2 \cdot C_6H_4 \cdot O \cdot C_6H_4Me$, prepared by the action of potassium *m*-cresoxide on *p*-bromonitrobenzene, is a pale yellow, crystalline substance which melts at 60—61° and boils at 230—233° under 30 mm. pressure. It furnishes a *sulphonic acid* which crystallises in white needles and melts at 135°; the *barium, strontium*, and *copper* salts are described.

p-*Aminophenyl* m-*tolyl ether* is stable when dry, but suffers partial

decomposition during desiccation; its *hydrochloride* forms colourless needles "which shrivel at 146°"; the *nitrate* and *sulphate* were also prepared. By the action of nitric acid on *p*-nitrophenyl *m*-tolyl ether, a *nitro*-derivative is produced as a yellow, crystalline solid which melts at 103—104°. E. G.

Influence of the CH_3 Group on Substitution in the Benzene Nucleus. JAN J. BLANKSMA (*Rec. trav. chim.*, 1902, 21, 327—338).—s-*Xylyl methyl ether*, prepared by methylating *s*-xylenol, is a colourless oil which boils at 193° and has an odour resembling that of anisole; it reacts with bromine in acetic acid to form *tribromo*-s-*xylyl methyl ether*, which separates from alcohol or acetic acid in colourless crystals and melts at 111°. *Trinitro*-s-*xylyl methyl ether* crystallises in colourless needles and melts at 127°; when heated with alcoholic ammonia in closed tubes at 100°, it is transformed into trinitro-*s*-xylidine. The latter, when boiled with alkali hydroxides in alcohol, gives off ammonia, but, owing probably to secondary reactions, no trinitro-*s*-xylenol could be isolated. 5-*Methylamino*-2 : 4 : 6-*trinitro*-m-*xylene*, obtained by the action of methylamine on trinitro-*s*-xylyl methyl ether, forms yellow crystals, melts at 164°, and on nitration furnishes the corresponding *nitroamine*, a colourless, crystalline substance which melts and decomposes at 181°. 5-*Ethylamino*-2 : 4 : 6-*trinitro*-m-*xylene*, similarly obtained, melts at 122°; the corresponding *nitroamine* melts at 85°. 2 : 4 : 6-*Trinitro*-m-*tolyl methyl ether*, obtained by the nitration of *m*-tolyl methyl ether, separates from alcohol in colourless crystals and melts at 92°; it is converted by ammonia into the corresponding 2 : 4 : 6-trinitro-*m*-toluidine, and by methylamine into 3-*methylamino*-2 : 4 : 6-*trinitrotoluene*, which forms yellow crystals, melts at 138°, and on nitration gives rise to the corresponding nitroamine. 3-*Ethylamino*-2 : 4 : 6-*trinitrotoluene* resembles its lower homologue, melts at 98°, and furnishes a *nitroamine* which forms colourless crystals and melts at 79°. Alcoholic solutions of these derivatives of the methyl ether of trinitro-*m*-cresol, as well as this ether itself, give red colorations with solutions of potassium cyanide, whilst the corresponding xylenol derivatives give no coloration with this reagent. When *as*-*m*-xylidine is treated with methyl iodide and the mixture of mono- and di-methyl derivatives thus obtained is nitrated, there is formed 4-*nitroamino*-2 : 5 : 6-*trinitro*-m-*xylene*, a colourless, crystalline substance which melts at 134°.

The reactions so far described indicate that the presence of two methyl groups in the *meta*-position to each other in a benzene nucleus facilitates nitration and bromination. When mesitylene is dissolved in sulphuric acid and the resulting sulphonic acid nitrated, trinitromesitylene is formed.

The author draws the conclusion, from the similar reactivities shown by the hydroxyl, amino-, and methyl groups, that a carboxyl or sulphonic group occupying an *ortho*- or *para*-position relatively to a methyl group should invariably undergo replacement on nitration or bromination, and, conversely, that where these acid groups occupy the same position relatively to halogen or methoxy-groups the acids are more stable (compare Klages and Lickroth, Abstr., 1899, i, 598). This

specific action of substituents with regard to entrant groups renders unnecessary any explanation based on stereochemical grounds.

T. A. H.

New Source of Thymol. J. A. Battandier (*J. Pharm. Chim.*, 1902, [vi], 16, 536).—About one-fourth of the essence of *Origanum floribundum* consists of thymol. G. D. L.

Phenyl Naphthyl Ethers and Hydroxyphenylnaphthalenes. Otto Hönigschmid (*Monatsh.*, 1902, 23, 823—828. Compare Abstr., 1901, i, 700).—Phenyl α-naphthyl ether and hydroxyphenyl-α-naphthalene are formed by the action of diazotised α-naphthylamine on phenol. Phenyl α-naphthyl ether crystallises in colourless leaflets, melts at 55°, is easily soluble in the ordinary organic solvents, but insoluble in aqueous alkali hydroxides. Hydroxyphenyl-α-naphthalene crystallises from methyl alcohol in long, glistening prisms containing CH_4O, which is lost on exposure to air; from light petroleum, it separates in nodular, crystalline aggregates and melts at 57°; the *benzoyl* derivative crystallises in small needles and melts at 83° (compare Hirsch, D.R.-P. 58001).

Phenyl β-naphthyl ether crystallises in thick, colourless needles and melts at 93°. Hydroxyphenyl-β-naphthalene crystallises in glistening leaflets, melts at 166—167°, is easily soluble in the ordinary organic solvents, and forms an *acetyl* derivative which crystallises in small, colourless needles and melts at 128°. G. Y.

Reduction of Diphenylene Oxide and the Dinaphthylene Oxides. Otto Hönigschmid (*Monatsh.*, 1902, 23, 829—835. Compare Abstr., 1901, i, 700).—Tetrahydrodiphenylene oxide is not reduced by sodium in boiling amyl alcohol solution. Tetrahydrodiphenylene oxide reacts with 1 mol. of bromine in chloroform solution with evolution of hydrogen bromide and formation of an oily *substitution* product.

With bromine in chloroform solution, octahydrodinaphthylene oxide forms a *dibromo*-substitution derivative, $C_{20}H_{18}OBr_2$, which crystallises in glistening leaflets, melts at 251°, is only slightly soluble in alcohol, and is not acted on by alcoholic potassium hydroxide or silver nitrate solutions.

On reduction with sodium and amyl alcohol, β-dinaphthylene oxide yields *tetrahydro-β-dinaphthylene oxide*, which crystallises in glistening leaflets or colourless needles, melts at 168°, and forms *dibromotetrahydro-β-dinaphthylene oxide*, $C_{20}H_{14}OBr_2$, crystallising from alcohol and melting at 137°. G. Y.

Anthesterol, a New Vegetable Cholesterol. Timothée Klobb (*Bull. Soc. chim.*, 1902, [iii], 27, 1229—1233. Compare Naudin, Abstr., 1884, 391).—*Benzoylanthesterol*, $C_{28}H_{47}\cdot OBz$, obtained together with an isomeride ? by benzoylating the crude substance (unnamed) described by Naudin (*loc. cit.*), separates from chloroform, on addition of alcohol, in colourless lamellæ, melts at 284—286°, sublimes unchanged, has $[\alpha]_D$ $+63\cdot9°$ ($c=2\cdot5$ per cent.) or $+59\cdot9°$ ($c=1\cdot25$

per cent.) in carbon tetrachloride, and is soluble in organic solvents with the exception of alcohol. When warmed with alcoholic potash, *anthesterol*, $C_{28}H_{48}O$, is obtained in the form of feathery tufts or fine needles; it melts at 221—223°, sublimes unchanged, has $[\alpha]_D$ +48·3° in ethylene bromide, and dissolves in organic solvents with the exception of methyl alcohol. It gives the usual colour reactions of the cholesterols, but unlike these furnishes, on addition of bromine, a mixture of *bromo*-derivatives, one of which crystallises in long needles, but has not been obtained pure. T. A. H.

Catechol from Coal-Tar. E. Börnstein (*Ber.*, 1902, **35**, 4324—4325).—The tar obtained by distilling certain Silesian and Rhenish-Westphalian coal at temperatures as low as possible contained small quantities of catechol. W. A. D.

Action of Chlorine and of Bromine on the Mononitroveratroles. H. Cousin (*Compt. rend.*, 1902, **135**, 967—969).—In order to ascertain the constitution of the trichloro- and tribromo-mononitroveratroles previously described (Abstr., 1902, i, 288), the action of chlorine and bromine on the mononitroveratroles [$C_6H_3(OMe)_2\cdot NO_2$, 1 : 2 : 3 and 1 : 2 : 4] has been studied. By the action of bromine on 3-nitroveratrole, a dibromonitroveratrole is formed (*Ann. Chim. Phys.*, 1898, [vii], **13**, 505), and by the further action of bromine in presence of sulphuric acid, yellowish needles of *tribromonitroveratrole*,

$$C_6Br_3(OMe)_2\cdot NO_2\ [4:5:6:1:2:3],$$

are obtained. This compound melts at 116—117°; it is insoluble in water, but soluble in alcohol, ether, or chloroform. It is identical with the substance obtained by the nitration of tribromoveratrole (obtained by methylating tribromoguaiacol), the constitution of which must therefore be $C_6H(OMe)_2Br_3$ [1 : 2 : 4 : 5 : 6]. The product obtained by brominating 4-nitroveratrole is a mixture of monobromonitroveratrole and tetrabromoveratrole.

Chlorine does not react in acetic acid solution on 3-nitroveratrole, but in presence of sulphuric acid a mixture of *dichloronitroveratrole* and *tetrachloroveratrole* is produced. The former crystallises in yellow leaflets, melts at 110—111°, and is insoluble in water or light petroleum, but soluble in alcohol, ether, or benzene. The tetrachloroveratrole forms white needles, melts at 88°, and is soluble in light petroleum. By the action of chlorine on 4-nitroveratrole in acetic acid solution in presence of sulphuric acid, a *dichloronitroveratrole* is formed which crystallises in long, yellowish needles, melts at 46—47°, and is insoluble in water, but soluble in the common organic solvents. No trichloronitroveratrole could be obtained by this process, but from analogy with the bromo-derivative it is probable that the trichloronitroveratrole previously obtained (*loc. cit.*) has the constitution $C_6Cl_3(OMe)_2\cdot NO_2$ [4 : 5 : 6 : 1 : 2 : 3]. J. McC.

Preparation of Aristol and its Derivatives. H. Cousin (*J. Pharm. Chim.*, 1902, [vi], **16**, 378—382).—Aristol (dithymol di-iodide), $C_{20}H_{24}O_2I_2$, is obtained by the action of a solution of iodine in potassium iodide on an alkaline solution of thymol. On employing,

in place of iodine, a concentrated solution of sodium hypochlorite, the corresponding *dichloride* is obtained. A *dibromide* may be similarly prepared. The dichloride decomposes at 195° without melting, is insoluble in water, but readily soluble in ether, chloroform, benzene, or carbon disulphide. W. P. S.

Constitution of Thebaol. ROBERT PSCHORR, C. SEYDEL, and W. STÖHRER (*Ber.*, 1902, 35, 4400—4410).—Thebaol (hydroxydimethoxyphenanthrene) was supposed by Freund (Abstr., 1897, i, 495) to contain one hydroxyl group in the meta-position, along with a methoxy-group in one benzene ring, and the remaining methoxy-group in the ortho-position in the third benzene ring. Thebaol, however, is readily oxidised in alkaline solution and therefore probably contains the hydroxyl in the para-position, whilst the acid thought by Freund to be *o*-hydroxyphthalic acid was probably *m*-hydroxyphthalic acid. In agreement with these considerations, it has been found by the synthesis of methylthebaol and acetylthebaolquinone from *vic.-o*-nitrovanillin methyl ether and nitro*iso*vanillin that thebaol has the constitution $\begin{array}{l} \mathrm{CH{:}CH{-}C{\cdot}CH{:}CH{\cdot}C{\cdot}CH{:}CH} \\ \mathrm{OMe{\cdot}C{:}C(OH){\cdot}C{-\!-\!-\!-}C{\cdot}CH{:}C{\cdot}OMe} \end{array}$.

vic.-o-Nitrovanillin methyl ether condenses with sodium *p*-methoxyphenylacetate in presence of acetic anhydride to form (α)-p-*methoxyphenyl*-vic.-2-*nitro*-3 : 4-*dimethoxycinnamic acid*,

$$\mathrm{OMe{\cdot}C}{<}\begin{array}{l}\mathrm{CH{-\!-\!-\!-\!-}CH} \\ \mathrm{C(OMe){:}C(NO_2)}\end{array}{>}\mathrm{C{\cdot}CH{:}C(CO_2H){\cdot}C_6H_4{\cdot}OMe},$$

which crystallises in long, dull yellow, pointed prisms melting at 230—231° (corr.). The *silver*, *calcium*, *barium*, and *lead* salts are all crystalline. This acid is accompanied by a small amount of 2-*nitro*-3 : 4 : 4'-*trimethoxystilbene*, $C_{17}H_{17}O_5N$, which crystallises in long, yellow, vitreous prisms melting at 156° (corr.). The nitro-acid is reduced by ferrous hydroxide in presence of ammonia to the corresponding p-*methoxyphenyl*-2-*amino*-3 : 4-*dimethoxycinnamic acid*, which crystallises in short, yellow prisms or tablets melting at 176—177° (corr.). The salts, both with bases and acids, are crystalline and well-defined. When heated with acetic anhydride, the base passes into 3-p-*methoxyphenyl*-7 : 8-*dimethoxy*-2-*carbostyril*, $C_{18}H_{17}O_4N$, which crystallises in colourless, pointed prisms melting at 282° (corr.) and forms solutions with a blue fluorescence. When the aminocinnamic acid is diazotised and the resulting solution heated, 3 : 4 : 6-*trimethoxyphenanthrene*-9-*carboxylic acid* is produced, which crystallises in slender, lustrous, faintly yellow needles melting at 203° (corr.) and forms soluble salts with the alkali and alkaline earth metals. When it is distilled under 100 mm. pressure, it yields *methylthebaol* as an oil which cannot be obtained crystalline. The *picrate* forms dark red needles melting at 109—110° (corr.). Bromine converts the trimethoxyphenanthrene into a *dibromo*-compound which crystallises in slender needles and melts at 122—123° (corr.).

Synthesis of Acetylthebaolquinone.—*vic.-o*-Nitro*iso*vanillin condenses with *p*-methoxyphenylacetic acid to form (α)-p-*methoxyphenyl*-2-*nitro*-3-*acetoxy*-4-*methoxycinnamic acid*, which crystallises in pointed prisms melting at 215° (corr.). p-*Methoxyphenyl*-2-*amino*-3-*hydroxy*-4-*methoxy*-

cinnamic acid, obtained by reduction, crystallises in needles melting at 150—152°, and rapidly becomes brown when exposed to the air in the moist state. When its solution in hydrochloric acid is treated with sodium nitrite, α-p-*methoxyphenyl*-3-*diazo*-2-*oxy*-4-*methoxycinnamic acid*, $OMe\cdot C{<}{\substack{CH—CH\\ CO\cdot C(N_2)}}{>}C\cdot CH{:}C(CO_2H)\cdot C_6H_4\cdot OMe$, separates; this substance crystallises in scarlet prisms which decompose violently at 145°, and is not decomposed when its neutral or acid solutions are boiled. The alkaline solution, however, yields, on boiling, 4-*hydroxy*-3 : 6-*dimethoxyphenanthrene*-9-*carboxylic acid*, which crystallises in brown, lustrous plates melting at 254—256° (corr.). The *acetyl* compound forms almost colourless crystals melting at 201—203° (corr.). The small amount of this substance which was obtained was converted by oxidation into a quinone, which was found to be identical with the acetylthebaolquinone prepared from thebaol by Freund.

A. H.

Identity of Thebaol Methyl Ether from Thebaine with 3:4:6-Trimethoxyphenanthrene. EDUARD VONGERICHTEN (*Ber.*, 1902, 35, 4410—4412. Compare preceding abstract).—Thebaol is converted by methylation into an oil which yields a picrate and dibromo-compound identical with the corresponding compounds prepared synthetically by Pschorr, Seydel, and Stöhrer. A. H.

Properties of Compounds of the Types $R\cdot CO\cdot O\cdot CH_2Cl$ and $(R\cdot CO\cdot O)_2CH_2$. MARCEL DESCUDÉ (*Bull. Soc. chim.*, 1902, [iii], 27, 1215—1219. Compare Abstr., 1902, i, 149, 339, 451, and 738).—Chloromethyl esters react with alcohols or their sodium derivatives to form dialkylformals, the corresponding alkyl ester or sodium salt respectively being obtained as a by-product.

Dibenzylformal, $CH_2(O\cdot CH_2Ph)_2$, obtained by the interaction of chloromethyl acetate with benzyl alcohol, is a colourless, rather viscous liquid, which boils at 280° with slight decomposition, has a sp. gr. 1·046 at 23°, and is decomposed by acids with the production of formaldehyde. One drop of dibenzylformal, when added to sulphuric acid, colours the latter an intense blood-red.

Methylene dibenzoate does not react with alcohols or their sodium derivatives. T. A. H.

Action of Fatty Amines on Methylene Dibenzoate. MARCEL DESCUDÉ (*Compt. rend.*, 1902, 135, 972—974).—The reaction between methylene dibenzoate and primary or secondary fatty amines proceeds in the same way as with ammonia (this vol., i, 72), so that mono- and di-alkylbenzamides are obtained. Tertiary amines do not react. The monomethyl- and monoethyl-benzamides have already been obtained. The monoalkylbenzamides are well-crystallised solids, whilst the dialkyl derivatives are oils of high boiling point. *Benzopropylamide*, $COPh\cdot NHPr^a$, forms quadratic pyramids which melt at 83°; it is insoluble in water and in light petroleum, but very soluble in alcohol and the common organic solvents. *Benzo*iso*butylamide* is easily soluble

in hot light petroleum, but almost insoluble in the cold. It melts at 54°, is insoluble in water, but soluble in organic solvents. *Benzobenzylamide* melts at 104—105° and may be crystallised from water, ether, or light petroleum.

By a secondary reaction which constantly takes place, the benzoates of the amines are also formed. These, as a rule, form well-defined, monoclinic crystals and will be described later. J. McC.

The Action of Anhydrous Nitric Acid on Diortho-substituted Amides. P. J. Montagne (*Rec. trav. chim.*, 1902, 21, 376—398).—2 : 4 : 6-*Trinitrobenzamide*, prepared by the action of aqueous ammonia on the corresponding chloride dissolved in benzene, forms yellow crystals and melts and decomposes at 264°; the corresponding *methylamide* and *dimethylamide* are crystalline and melt at 285° and 144° respectively. The first of these amides, when dissolved in anhydrous nitric acid, furnishes 2 : 4 : 6-trinitrobenzoic acid, the second is converted into a colourless, crystalline *substance* which melts at 173° and is probably a nitroamide of the constitution $C_6H_2(NO_2)_3\cdot CO\cdot NMe\cdot NO_2$, since it reproduces the original methylamide when warmed with dilute sulphuric acid, whilst the third is unaltered.

2 : 4 : 6-*Trichloro-3-nitrobenzoic acid*, prepared from aniline as a starting point by Meyer and Sudborough's method (Abstr., 1895, i, 93), forms monoclinic crystals [$a : b : c = 0·6540 : 1 : 0·3333$; $\beta = 76°5'30''$]; it combines with varying quantities of its solvents, but melts when anhydrous at 169·25°. When treated with phosphorus pentachloride dissolved in phosphorus oxychloride, it furnishes 2 : 4 : 6-*trichloro-3-nitrobenzoic chloride*, which separates from light petroleum in crystals melting at 96°, is not decomposed by water, but in benzene solution is converted by aqueous ammonia into the corresponding amide; this forms large, monoclinic tablets [$a : b : c = 1·5933 : 1 : 1·0023$; $\beta = 65°2'10''$] and melts at 228·5°. The corresponding *methylamide* separates from mixtures of acetone and benzene in monoclinic prisms [$a : b : c = 1·1295 : 1 : 0·7112$; $\beta = 74°15'46''$] and melts at 217·25°. The *dimethylamide* separates from benzene on addition of light petroleum in small crystals belonging to the monoclinic system [$a : b : c = 1·1164 : 1 : 1·1171$; $\beta = 50°5'25·5''$]; it melts at 111·25°. The simple amide is converted by anhydrous nitric acid into 2 : 4 : 6-trichloro-3-nitrobenzoic acid, whilst the methylamide furnishes with this reagent the *nitromethylamide*, which separates from benzene and light petroleum in monoclinic crystals [$a : b : c = 0·3009 : 1 : 0·3937$; $\beta = 8°28'44''$], melting at 118·5°, and with dilute sulphuric acid partly regenerates the original methylamide, but is also partially converted into trichlorobenzoic acid. The dimethylamide is not acted on by anhydrous nitric acid. These results are in accordance with the author's view that the cause of the inhibiting action of groups in the *ortho*-position relatively to the amino-group on the reactivity of the latter is stereochemical. It is pointed out that the 2 : 4 : 6-trichloro-3-nitrobenzoic acid described by Beilstein (Handbuch 2, 1241) is probably 2 : 4 : 5-trichloro-3-nitrobenzoic acid.

T. A. H.

Additive Products of Various Acids. SEBASTIAAN HOOGEWERF and WILLEM ARNE VAN DORP (*Rec. trav. chim.*, 1902, **21**, 349—365. Compare Abstr., 1899, i, 672).—The following acids combine with one mol. of sulphuric acid to form colourless additive *compounds* which crystallise in needles: *m*-bromobenzoic, *o*-toluic, *p*-toluic, 2 : 4-dimethylbenzoic, 3 : 4-dimethylbenzoic, 2 : 5-dimethylbenzoic, 2 : 4 : 5-trimethylbenzoic, *p*-nitrocoumaric, and phthalic.

The following compounds of two organic acids have been obtained: benzoic acid (1 mol.) with dichloroacetic acid (1 mol.), coumaric acid (1 mol.) with dichloroacetic acid (1 mol.), cinnamic acid (2 mols.) with trichloroacetic acid (1 mol.), and camphoric acid (2 mols.) with acetic acid (1 mol.), with chloroacetic acid (1 mol.), with dichloroacetic acid (1 mol.), with trichloroacetic acid (1 mol.), and with *iso*butyric acid (1 mol.).

The following phenols combine with phosphoric acid (1 mol.) to form crystalline *derivatives*: phenol, *p*-bromophenol, quinol, and *p*-cresol.

The following ketones furnish *derivatives* containing 1 mol. of sulphuric acid; *m*-xylyl methyl ketone, ψ-cumyl methyl ketone, and benzil.

Vanillin combines with 1 mol., and piperonal with 3 mols., of sulphuric acid. ψ-Cumenesulphonic acid (1 mol.) combines with 1 mol. of phosphoric acid.

The following acids do not form additive compounds of this character: 2 : 4 : 6-trimethylbenzoic, 2 : 3 : 5 : 6-tetramethylbenzoic, 2 : 4 : 5 : 6-tetramethylbenzoic, *o*-, *m*-, and *p*-chlorobenzoic, 2 : 4 : 6-trichlorobenzoic, *o*- and *p*-bromobenzoic, 2 : 4-dibromobenzoic, and 3 : 5-dibromobenzoic.

The methylbenzoic acids furnish compounds with sulphuric acid except in cases where the two *ortho*-positions relative to the carboxyl are occupied by methyl groups; this is in accordance with Victor Meyer's rule (Abstr., 1894, i, 463, and 1895, i, 466); it should also follow that such acids are more stable towards sulphuric acid, but this is not the case, since 2 : 4 : 6-trimethylbenzoic, 2 : 4 : 5 : 6-tetramethylbenzoic, and 2 : 3 : 5 : 6-tetramethylbenzoic acids are decomposed by sulphuric acid, furnishing carbon dioxide and the corresponding hydrocarbon, whilst mesitylenesulphonic acid is decomposed even by boiling acetic acid. Similarly, ketones of the type R·CO·Me, where R is a methylated phenyl, are stable towards sulphuric acid except in such cases as mesityl, duryl, and *iso*duryl methyl ketones. It appears, therefore, that the occurrence of two methyl groups in the *ortho*-position relatively to a reacting group in an aromatic nucleus facilitates rather than inhibits reactivity (compare V. Meyer, Abstr., 1895, i, 466; Klages and Lickroth, *ibid.*, 1899, i, 598; Weiler, *ibid.*, 1899, i, 703, and Blanksma, *ibid.*, 1902, i, 600), whilst the stability is increased by substituent haloids in these positions (compare Blanksma, this vol., i, 158).

The additive compounds may be regarded as oxonium derivatives and represented by formulæ such as $H_2\colon OPh\cdot O\cdot PO(OH)_2$, or it may be supposed that in their formation such double oxygen linkings as $\colon C\colon O$ and $\vdots P\colon O$ become single, when formulæ such as $Ph\cdot O\cdot P(OH)_4$

are obtained; the information at present available is insufficient to decide between these representations. T. A. H.

Chemical Action of Light. Giacomo Ciamician and Paul Silber (*Ber.*, 1902, 35, 4128—4131).—As a result of the continuation of their former work (compare Abstr., 1901, i, 329 and 390; 1902, i, 433), the authors find that, under the influence of light, unsaturated compounds exhibit a decided tendency to polymerise.

It has been already shown by Bertram and Kürsten that when dry cinnamic acid is exposed to sunlight it is rapidly and almost completely transformed into α-truxillic acid. The authors find, however, that when an absolute alcoholic solution of cinnamic acid is left in the light for nearly five months, about half the acid is converted into the ethyl ester, the rest being unchanged; no sign of truxillic acid could be found. When suspended in, and partially dissolved by, paraldehyde, cinnamic acid is, to some extent, polymerised into α-truxillic acid, but the authors consider that it is only the undissolved cinnamic acid which undergoes this change.

Under the influence of light, a solution of stilbene in benzene assumes a pale yellow colour, part of the stilbene being polymerised into a compound having the doubled formula, $C_{28}H_{24}$, as is shown by a cryoscopic molecular weight determination in naphthalene solution. This compound crystallises from ether in colourless prisms, and in alcoholic solution is stable towards permanganate.

Exposed to light in either alcohol or paraldehyde solution, coumarin undergoes partial polymerisation into a dipolymeride, $C_{18}H_{12}O_4$, which is probably identical with Dyson's dihydrocoumarin and separates from the solution in colourless, well-formed crystals melting at 262°. T. H. P.

Action of Hydrogen on *iso*Salicylic Acid in Alkaline Solution. Heinrich Brunner (*Chem. Zeit.*, 1902, 26, 1123—1124. Compare *ibid.*, 541).—By treating salicylic acid with bromine and aqua regia, a dibromosalicylic acid is obtained which differs from the ordinary dibromosalicylic acid, but can be converted into it by the action of hydrogen; this acid is believed to be a *dibromo*iso*salicylic acid.* When treated with aqua regia, salicylic acid is partly changed into an isomeric acid which crystallises in the triclinic system, whereas salicylic acid is monoclinic. The *iso*-acid can be converted into, and recovered from, its salts and esters. With hydrazine hydrate, *iso*salicylic acid gives a compound

$$C_7H_6O_3,N_2H_4,$$

whilst salicylic acid gives a compound $(C_7H_6O_3)_2,N_2H_4$. With phenylcarbimide, the *iso*-acid does not react at 100°, but the normal acid yields a urethane. On heating salicylic acid or its potassium salt under pressure at 180—200° for 2 hours, it remains unchanged, but the *iso*-acid sinters to a reddish-grey mass with formation of phenol and carbon dioxide. On reducing *iso*salicylic acid with sodium amalgam or, better, sodium hydroxide and aluminium powder, a blue liquid is obtained which becomes red with acids; a similar reaction is observed on distilling it with lime. A mixture of salicylic and nitrosalicylic acids

gives the same colorations when similarly treated. Further, this reaction is given by the sublimate from a mixture of salicylic and nitrosalicylic acids; when alone, the latter acid cannot be sublimed. Salicylic acid gives a similar colour reaction when mixed with *o*- or *p*-nitrophenol, but not with the *m*-isomeride. K. J. P. O.

The Three Isomeric Ethyl Benzylideneanilineacetoacetates. ROBERT SCHIFF (*Ber.*, 1902, **35**, 4325—4328).—A reply to Rabe (this vol., i, 62), in which the existence of the three forms of ethyl benzylideneacetoacetate is maintained; it is pointed out that although these derivatives are at first dimolecular in benzene solution, they are suddenly resolved, after about 10 minutes, into single molecules, as shown by a halving of the observed molecular weight.

W. A. D.

Dissociation of Ethyl Benzylideneanilineacetoacetates. WILHELM BILTZ (*Ber.*, 1902, **35**, 4438—4440. Compare Rabe, this vol., i, 62).—The molecular weights of the compounds described by Schiff (Abstr., 1898, i, 237, and preceding abstract) as melting at 77—78° and at 103—104° have been determined by the cryoscopic method in naphthalene solution and by the ebullioscopic method in benzene solution. In nearly all cases, the results come below those required for the compound $C_{19}H_{21}O_3N$, indicating that partial dissociation occurs. The compound melting at 103—104° gives normal results when freshly dissolved in naphthalene, but the numbers quickly diminish. The numbers obtained with the strongly associating solvent benzene are, as a rule, higher than those obtained with naphthalene.

J. J. S.

Condensation of Naphthalaldehydic Acid with Ketones. JOSEF ZINK (*Monatsh.*, 1902, **23**, 836—841. Compare Abstr., 1902, i, 31).—Naphthalidomethyl phenyl ketone reacts with methylamine yielding *methyl phenacylnaphthalimidine*, $CO<\substack{C_{10}H_6\\NMe}>CH\cdot CH_2\cdot COPh$, which crystallises in white needles, melts at 95—100°, is easily soluble in the ordinary organic solvents, does not form an acetyl derivative, and does not undergo isomeric change when boiled with alkalis or alcoholic hydrochloric acid.

Attempts to methylate phenacylnaphthalimidine by heating with methyl iodide, with or without addition of potassium hydroxide, resulted in the formation of the yellow isomeride. When heated with acetic anhydride, phenacylnaphthalimidine yields an *acetyl* derivative crystallising in white needles and melting at 145°.

As the yellow isomeride does not undergo Hofmann's reaction with bromine and is not attacked by nitrous acid, it cannot be represented by the formula previously suggested.

Naphthalidomethyl n-*butyl ketone*, formed by the condensation of naphthalaldehydic acid with methyl *n*-butyl ketone, crystallises in white needles, melts at 75°, is soluble in the usual organic solvents, and, when warmed with aqueous alkalis, dissolves and decomposes with formation of methyl butyl ketone. G. Y.

Hydroxyphenanthrenecarboxylic Acids. ALFRED WERNER and J. KUNZ (*Ber.*, 1902, **35**, 4419—4429).—*3-Hydroxyphenanthrene-2-carboxylic acid* is produced when the dry sodium derivative of 3-phenanthrol is heated with excess of carbon dioxide at 240—250° under 10—30 atm. pressure for 6 hours. It crystallises in short, yellow prisms, melts and decomposes at 303°, and dissolves in 80 parts of boiling acetone. The *calcium, barium, lead, ferric,* and *ferrous* salts are described. The *acetyl* derivative is colourless and melts at 207—208°, the *methyl* ester crystallises in yellowish needles melting at 171°.

The isomeric *2-hydroxyphenanthrene-3-carboxylic acid*, obtained in a similar manner from the sodium derivative of 2-phenanthrol, crystallises from a mixture of benzene and acetone in long, yellow needles melting and decomposing at 277° and is soluble in about 40 parts of boiling acetone. The *calcium, barium, lead, ferric,* and *errous* salts are described. The *acetyl* derivative melts and decomposes at 210°, and is only sparingly soluble in hot glacial acetic acid. The *methyl* ester melts at 126°. The dry powdered acids and also 1 per cent. aqueous solutions of the sodium salts of the acids have strong antiseptic properties and readily destroy *Staphylococcus pyogenes.* Subcutaneous injections of the acids mixed with 1 per cent. peptone solution caused the death of white mice.

An apparatus is described for use in heating different substances with carbon dioxide under pressure. J. J. S.

Salts of Indigotin. ARTHUR BINZ and AUGUST KUFFERATH (*Annalen*, 1902, **325**, 196—204).—Although it has been known that indigotin dissolves in a mixture of glacial acetic and sulphuric acids, whereas it is insoluble in acetic acid alone, yet the salts of indigotin have not hitherto been isolated. *Indigotin hydrochloride*, $C_{16}H_{10}O_2N_2,HCl$, is prepared by passing dry hydrogen chloride into a suspension of indigo in acetic acid, benzene, or chloroform, when it dissolves, forming a deep blue solution; from the acetic acid solution, ether precipitates the salt as lustrous leaflets, well-formed, six-sided prisms being also obtained by spontaneous crystallisation; by water, they are completely hydrolysed. The *hydrobromide* is a similar compound; the hydriodide could not be prepared. The *platinichloride*, $(C_{16}H_{10}O_2N_2)_2,H_2PtCl_6$, is prepared by mixing acetic acid solutions of the hydrochloride and of chloroplatinic acid, when the salt separates in microscopic, blue-black, rhombic plates. *Indigotin sulphate*, $C_{16}H_{10}O_2N_2,H_2SO_4$, is very easily obtained by dissolving indigo powder in a mixture of acetic and sulphuric acids (5 vols. of acetic to 1 vol. of sulphuric acid); when kept, or on addition of ether, the salt crystallises in deep blue needles and is quite stable in the air, but decomposed by water, alcohol, or acetic acid. The *hydrogen sulphate*, $C_{16}H_{10}O_2N_2,2H_2SO_4$ (Badische Anilin- and Soda-Fabrik, D.R.-P. 121450), is obtained as a hygroscopic mass of slender needles when finely powdered indigo is treated with sulphuric acid of 60° Bé.

It is suggested that in indigo analysis a mixture of acetic and sulphuric acids should be used instead of acetic acid to extract the indigotin. K. J. P. O.

New Compound of Acetylsalicylic Acid. EMIL UHLFELDER and LUDWIG VANINO (*Chem. Centr.*, 1902, ii, 1314; from *Pharm. Zeit.*, 47, 847).—*Acetylsalicylic acid peroxide*, prepared by the action of hydrogen peroxide on a solution of acetylsalicylic chloride in acetone at 0° in presence of pyridine, melts at 109—110°, has not been made to detonate by heating in a capillary tube, and does not give a violet coloration with ferric chloride. E. W. W.

The α-Phenylphthalimide of Kuhara and Fukui. SEBASTIAAN HOOGEWERF and WILLEM ARNE VAN DORP (*Rec. trav. chim.*, 1902, **21**, 339—348).—It is shown that the substance described by Kuhara and Fukui (Abstr., 1902, i, 34) as α-phenylphthalimide is in reality phthalyldiphenyldiamide (Van der Meulen, Abstr., 1897, i, 281). The true α-phenylphthalimide has already been obtained and described by Van der Meulen (*loc. cit.*) under the name phthalylphenyl*iso*imide. T. A. H.

Hydration of o-Hydroxybenzoylformic Acid. PAUL FRITSCH (*Ber.*, 1902, **35**, 4346. Compare Stoermer, this vol., i, 457).—When *o*-hydroxybenzoylformic acid is dissolved in ether and moistened with a few drops of water, it yields, on evaporation of the ether, a syrup which deposits flat, prismatic crystals of the acid; these melt at 41—42° and have the composition of a hydrated acid, $OH\cdot C_6H_4\cdot C(OH)_2\cdot CO_2H$. T. M. L.

Abnormal Course of Michael's Condensation. JOSEF SVOBODA (*Monatsh.*, 1902, **23**, 842—864. Compare Skraup, Abstr., 1901, i, 226).—The condensation of ethyl citraconate and the sodium derivative of ethyl methylmalonate leads to the formation of a colourless *oil*, which boils at 198—201° under 15 mm. pressure and is probably ethyl methylketo*cyclo*pentanetricarboxylate, $CO<\begin{matrix}CH_2\cdot C(CO_2Et)_2\\ | \\ CH_2\cdot CMe\cdot CO_2Et\end{matrix}$. With phenylhydrazine, the oil forms water and a viscous, red mass, probably the phenylhydrazone.

On hydrolysis, the tricarboxylic acid loses $2CO_2$ and yields *methylketo*cyclo*pentanecarboxylic acid*, $C_5H_6MeO\cdot CO_2H$; this is obtained in two modifications, one of which is extracted by ether from the aqueous solution. The acid, soluble in ether, is a thick, yellow oil which distils at 128° under 15 mm. pressure. Before distillation, it has $[\alpha]_D$ $+36{\cdot}66°$ (in another preparation $[\alpha]_D$ $+18{\cdot}73°$), but after distillation the acid is inactive. The *brucine* salt, $C_7H_{10}O_3,C_{23}H_{26}O_4N_2,4H_2O$, crystallises in long prisms, melts at 85°, loses $4H_2O$ at 105°, and melts when anhydrous at 143°. The *calcium* salt, $(C_7H_9O_3)_2Ca,4H_2O$, crystallises in rhombic prisms, and in aqueous solution gives a white precipitate with silver nitrate or mercuric chloride solution. The *ethyl* ester is a colourless oil and distils at 237° under 732 mm. or at 118° under 15 mm. pressure; its *oxime* crystallises in rhombic plates, melts at 52°, and is easily soluble in water, alcohol, or ether.

With phenylhydrazine, the ethyl ester forms a *substance*, $C_{13}H_{14}ON_2$(?), which separates from alcohol as a brownish-yellow, amorphous powder and melts at 143°.

The modification of methylketo*cyclo*pentanecarboxylic acid, soluble in water and not extracted by ether, forms a thick, yellow syrup, which can be distilled under reduced pressure and is optically inactive. The *brucine* salt, $C_7H_{10}O_3,C_{23}H_{26}O_4N_2$, crystallises in delicate needles and melts at 118°; the *silver* salt forms a white, amorphous precipitate. The *ethyl* ester is a colourless liquid, boils at 120° under 15 mm. pressure, and forms an *oxime* which crystallises in rhombic plates and melts at 52°. With strychnine, the acid forms a *derivative* which crystallises in needles, melts at 227°, and is hydrolysed when heated with water. G. Y.

Crystallography of some Lichenic Acids. HUBERT KAPPEN (*Zeit. Kryst. Min.*, 1902, **37**, 151—170).—Detailed crystallographic and optical determinations are given for the following substances: atranoric acid, zeorin, usnic acid, pinastric acid, placodiolin, vulpic acid, vulpic anhydride, sodium vulpinate, propylpulvic acid, ethylpulvic acid, calycin, stictaurin, and rhizocarpic acid. L. J. S.

Nitro-derivatives of *iso*Vanillin. ROBERT PSCHORR and W. STÖHRER (*Ber.*, 1902, **35**, 4393—4399).—The constitutions of the three mononitro-derivatives of *iso*vanillin were ascertained by the comparison of their methyl ethers with the nitro-derivatives of methylvanillin, the constitution of which is already known (Abstr., 1900, i, 178). 2 : 6-*Dinitro*iso*vanillin*,

$$CHO\cdot C_6H(NO_2)(OH)(OMe)\cdot NO_2\ [1:2:3:4:6],$$

is formed when *iso*vanillin is carefully nitrated below 0° with concentrated nitric acid, or below 10° with dilute acid, and crystallises in colourless needles melting at 164—165° (corr.). It is also formed by the further nitration of both 2- and 6-nitro*iso*vanillin. The *phenylhydrazone* forms dark red plates melting at 185° (corr.).

The nitration of *iso*vanillin in acetone solution below 10° leads to the formation of s-o-*nitro*iso*vanillin*,

$$CHO\cdot C_6H_2(OH)(OMe)\cdot NO_2\ [1:3:4:6],$$

and vic.-o-*nitro*iso*vanillin*, $CHO\cdot C_6H_2(OH)(OMe)\cdot NO_2$ [1 : 3 : 4 : 2]. The symmetrical compound is precipitated from the solution of its sodium salt by carbon dioxide and crystallises in yellow needles melting at 189° (corr.). The *phenylhydrazone* forms dark red, lustrous plates melting at 200—201°. The methyl ether is identical with *s-o*-nitrovanillin methyl ether. *vic.-o*-Nitro*iso*vanillin crystallises in almost colourless plates melting at 148—149° (corr.), and is more soluble than its isomeride. The *phenylhydrazone* crystallises in dark violet, fascicular groups of needles melting at 157—158° (corr.). *Acetyl*iso*vanillin* is best obtained by the direct action of acetic anhydride, and crystallises in needles melting at 64°. On nitration with fuming nitric acid, it yields 5-*nitroacetyl*iso*vanillin*,

$$CHO\cdot C_6H_2(OAc)(OMe)\cdot NO_2\ [1:3:4:5],$$

which crystallises in faintly yellow needles melting at 86° (corr.); the *phenylhydrazone* forms yellow needles melting at 165° (corr.). 5-*Nitro*iso*vanillin* crystallises in colourless needles melting at 113° (corr.). *Benzoyl*iso*vanillin* crystallises in colourless prisms melting at 75° (corr.), yields a *phenylhydrazone* melting at 187° (corr.), and is

converted by nitration into 5-*nitrobenzoylisovanillin*, which crystallises in colourless needles melting at 120—121° (corr.); the *phenylhydrazone* melts at 205—206° (corr.). 5-Nitro*iso*vanillin and 5-nitrovanillin both yield the same *methyl ether*, which crystallises in colourless needles melting at 90—91° (corr.); the *phenylhydrazone* forms yellow plates and melts at 108—110°. A. H.

Preparation of *o*-Aminobenzophenone Derivatives. FRITZ ULLMANN and H. BLEIER (*Ber.*, 1902, 35, 4273—4280).—A method of preparing *o*-aminobenzophenone derivatives from *o*-aminobenzoic acid has been devised. *p*-Toluenesulphone-*o*-aminobenzoic acid, which is easily prepared, is converted into the acid chloride, and the latter, without being isolated, treated with benzene and aluminium chloride, when the benzophenone derivative is formed. p-*Toluenesulphone-o-aminobenzoic acid*, $C_7H_7 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot CO_2H$, is prepared by adding *p*-toluenesulphonic chloride to a warm solution of *o*-aminobenzoic acid in sodium carbonate; it crystallises in white needles melting at 217°, and when treated with methyl sulphate in sodium hydroxide solution yields *methyl* p-*toluenesulphone*-o-*methylaminobenzoate*, which forms lustrous crystals melting at 94°. p-*Toluenesulphone*-o-*aminobenzophenone*, $C_7H_7 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot COPh$, is obtained from the acid just described by treating it in benzene solution successively with phosphoric chloride and aluminium chloride; it crystallises in star-shaped aggregates melting at 127°, and is soluble in alkali hydroxides; the yield amounts to 75 per cent. of the theoretical; at the same time, there is formed a small amount of phenyl *p*-tolyl sulphone (m.p. 124°), the proportion of which increases with increase of the amount of aluminium chloride used. p-*Toluenesulphone*-o-*methylaminobenzophenone*, prepared by the action of methyl sulphate on an alkaline solution of the benzophenone, forms colourless crystals melting at 124°. *o*-Aminobenzophenone is readily obtained by hydrolysing with warm sulphuric acid the sulphone, which need not for this purpose be purified. *o-Methylaminobenzophenone* is prepared in an exactly similar manner from toluenesulphone-*o*-methylaminobenzophenone; it forms yellow crystals melting at 66°. p-*Toluenesulphone*-o-*aminophenyl* p-*tolyl ketone*, $C_7H_7 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot CO \cdot C_7H_7$, is prepared from toluenesulphone-*o*-aminobenzoic acid, which is treated with phosphoric chloride and aluminium chloride in toluene solution; it forms white crystals melting at 123°, and on hydrolysis gives *o*-aminophenyl *p*-tolyl ketone (m. p. 95°; Kippenberg, Abstr., 1897, i, 421). *o*-Aminophenyl α-naphthyl ketone (m. p. 140·5°) was prepared by treating a solution in carbon disulphide of the toluenesulphone acid and naphthalene with phosphoric chloride and aluminium chloride. p-*Toluenesulphone-2-amino-4'-methoxybenzophenone*,

$$C_7H_7 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot OMe,$$

is extremely easily prepared from toluenesulphoneaminobenzoic acid and anisole by this method; it crystallises in leaflets melting at 143°, and by heating with a mixture of acetic and sulphuric acids is converted into *2-amino-4'-methoxybenzophenone*; which crystallises in yellow, star-shaped aggregates melting at 76°. 3-*Methoxyfluorenone*, $CO<\begin{matrix}C_6H_4\\|\\C_6H_3 \cdot OMe\end{matrix}$, is prepared from the substance last mentioned by

diazotising and boiling the resulting solution; it forms yellow leaflets melting at 99° and dissolves in sulphuric acid to a violet-red solution. 3-*Hydroxyfluorenone* is obtained by heating the methoxy-derivative with aluminium chloride at 150°; it forms yellow crystals melting at 225° and dissolves in sodium hydroxide with an orange-red, and in sulphuric acid with a dirty-violet, coloration. K. J. P. O.

Derivatives of Phenol-Ketones. Pietro Bartolotti and Adolfo Linari (*Gazzetta*, 1902, 32, ii, 271—276).—*Phenyl bromo-2-hydroxy*-p-*xylyl ketone*, $COPh\cdot C_6HBrMe_2\cdot OH$, separates from alcohol in large, colourless crystals melting at 115—116°.

Phenyl bromo-4-hydroxy-o-*xylyl ketone* is deposited from alcohol in very vivid cedar-yellow crystals melting at 134—135°. It yields two oximes: the syn.-*oxime*, $\begin{matrix}Ph\cdot C\cdot C_6H_2Me_2\cdot OH\\ \Vert \\ N\cdot OH\end{matrix}$, which separates from dilute alcohol in large, anhydrous crystals melting at 140·5—141·5° and is transformed, either by heating at 170° or by the action of gaseous hydrogen chloride, into the anti-*compound*, $\begin{matrix}OH\cdot C_6H_2Me_2\cdot C\cdot Ph\\ \Vert \\ N\cdot OH\end{matrix}$, which is deposited from dilute alcohol in silky needles melting at 165—166°.

Phenyl bromo-o-*hydroxytolyl ketone*, $COPh\cdot C_6H_2BrMe\cdot OH$, separates from alcohol in white, silky needles melting at 130—131°.

The *oxime* of 1 : 2 : 3-*hydroxydimethoxybenzophenone*,

$$OH\cdot N\colon CPh\cdot C_6H_2(OMe)_2\cdot OH,$$

separates from dilute alcohol in white, anhydrous crystals which melt at 137—138° and are readily soluble in alcohol, ether, or chloroform.

T. H. P.

Condensation of Fluorene with Benzoic Chloride. Max Fortner (*Monatsh.*, 1902, 23, 921—928. Compare Goetz, Abstr., 1902, i, 372).—3-(or 4)-*Benzoylfluorene*, $C_{13}H_9Bz$, prepared from fluorene and benzoic chloride in presence of aluminium chloride in carbon disulphide solution, crystallises in pale yellow, glistening needles, melts at 124—126°, is easily soluble in benzene or carbon disulphide, but less so in alcohol or glacial acetic acid, and, with concentrated sulphuric acid, gives an intense yellow coloration, disappearing on addition of water. The *oxime*, $C_{20}H_{15}ON$, crystallises in rose-tinted needles, sinters at 199°, and melts at 205°. The *phenylhydrazone*, $C_{26}H_{20}N_2$, crystallises in matted, yellow needles, melts at 156°, and is easily soluble in alcohol.

On distillation with zinc dust, benzoylfluorene is converted into 3-(or 4)-benzylfluorene, $C_{13}H_9\cdot CH_2Ph$, which crystallises in glistening, white leaflets and melts at 104—106° (compare Goldschmidt, *Monatsh.*, 1881, 2, 443).

By the action of sodium dichromate in glacial acetic acid solution, benzoylfluorene is oxidised to 3-(or 4)-*benzoylfluorenone*, $CO<\begin{matrix}C_6H_4\\ | \\ C_6H_3Bz\end{matrix}$, which crystallises in glistening, yellow leaflets, melts at 175—177°, is sparingly soluble in alcohol, but easily so in benzene or chloroform, and gives an intense reddish-yellow coloration with concentrated

sulphuric acid. The *dioxime* crystallises in small, yellow needles and melts at 228—230°. The *monoxime* crystallises in pale yellow leaflets, sinters at 185°, and melts at 199°. The *diphenylhydrazone* forms yellow, flocculent crystals, melts at 83°, and dissolves in sulphuric acid to a deep wine-red solution which becomes brown on addition of ferric chloride. The *monophenylhydrazone* crystallises in matted, glistening, lemon-yellow needles and melts at 183°. G. Y.

Action of Bromine on Di-*p*-hydroxystilbene. THEODOR ZINCKE and K. FRIES (*Annalen*, 1902, **325**, 19—44).—Dihydroxystilbene is best prepared by the action of iron powder, instead of zinc dust, on diphenoltrichloroethane (compare Elbs, Abstr., 1889, 997, and 1893, i, 271); with this modification, the yield is 40 per cent. of the theoretical. On treatment with hydrogen bromide in acetic acid solution, dihydroxystilbene is converted into a *substance*, $C_{14}H_{12}O_2$, which forms an amorphous, white powder sintering at 190° and melting and decomposing at 250°; its *acetyl* derivative, $C_{14}H_{10}O_2Ac_2$, is an amorphous powder. On reducing the amorphous substance with hydriodic acid and phosphorus, a very small quantity of di-*p*-hydroxydibenzyl (? m. p. 187°) is obtained. Stilbene dibromide (m. p. 237°) is prepared by brominating the product of the distillation of this compound with zinc dust. Tetrabromodi-*p*-hydroxydibenzyl ψ-dibromide (tetrabromodi-*p*-hydroxystilbene dibromide),

$$C_2H_2Br_2\left(CH{<}{\begin{matrix}CH{:}CBr\\CH{:}CBr\end{matrix}}{>}CO\right)_2 \quad \text{or} \quad C_2H_2Br_2\left(C{<}{\begin{matrix}CH{\cdot}CBr\\CH{:}CBr\end{matrix}}{>}C{\cdot}OH\right)_2,$$

is prepared by treating dihydroxystilbene suspended in glacial acetic acid with a large excess of bromine; it forms colourless, insoluble needles, melting and decomposing at 265°, and is very readily oxidised; from the acetic acid mother liquor of the last-mentioned substance, tetrabromodi-*p*-hydroxybenzil, $C_{14}H_6O_4Br_4$, is obtained as a pale yellow powder, which does not change at 270° and is soluble in alkalis; with *o*-phenylenediamine, it gives a quinoxaline melting at 240°. When the hexabromide is reduced with zinc and acetic acid, *tetrabromodihydroxystilbene*, $C_{14}H_8O_2Br_4$, is formed, which crystallises in long needles melting at 269° and is soluble in alkalis, these solutions being readily oxidised. The *diacetyl* derivative, $C_{14}H_6O_2Br_4{\cdot}Ac_2$, crystallises in prisms terminated by pyramids melting at 241°. Tetrabromodi-*p*-hydroxydibenzil is formed in considerable quantity together with the stilbene derivative.

Tetrabromostilbenequinone (*tetrabromodibenzylidenequinone*),

$$C_2H_2\left({:}C{<}{\begin{matrix}CH{:}CBr\\CH{:}CBr\end{matrix}}{>}CO\right)_2,$$

is prepared either by boiling the ψ-hexabromide with dilute acetone, when hydrogen bromide is eliminated, or by oxidising the tetrabromodihydroxystilbene with nitric acid; the quinone is a reddish powder closely resembling red phosphorus, crystallises from nitrobenzene in steel-blue needles, and at 300° changes into a pale yellow, insoluble *compound*; when heated with an acetic acid solution of hydrogen bromide it is reconverted into the hexabromide, and on reduction gives the tetrabromide. With alkali hydroxides, the quinone yields *additive* products, $C_{14}H_6O_2Br_4,NaOH$ and $C_{14}H_6O_2Br_4,KOH$, which form dark-

green powders, and can also be obtained by the action of the alkalis on the hexabromide, and by alkalis and air on tetrabromodihydroxystilbene; by acids, this compound is converted into the quinone; on prolonged heating with dilute alkalis, the green compounds are changed into a mixture of tetrabromodihydroxystilbene and tetrabromodihydroxydibenzil.

The quinone forms a series of additive products with methyl alcohol, acetic acid, and acetic anhydride, each of which exists in two forms; these are respectively the derivatives of hydrobenzoin and *iso*hydrobenzoin. The *dimethyl ether* of tetrabromodi-*p*-hydroxyhydrobenzoin, $C_2H_2(OMe)_2\left(C{<}{\begin{smallmatrix}CH\cdot CBr\\CH{:}CBr\end{smallmatrix}}{>}C\cdot OH\right)_2$, is obtained by heating the quinone with methyl alcohol under pressure at 100° until solution is complete; it crystallises in prisms with acetic acid and melts at 209°; the iso*ether*, which remains dissolved in the acetic acid mother liquor from the normal ether, crystallises in cubes melting at 160°; both ethers are soluble in alkalis.

Tetrabromodi-p-*hydroxyhydrobenzoin diacetate*, $C_{14}H_8O_4Br_4Ac_2$, is prepared by boiling the quinone with acetic acid and sodium acetate until dissolution is complete; it is separated from its isomeride by repeated crystallisation from acetic acid, from which it crystallises more rapidly in small plates melting at 218°; the iso-*compound* crystallises with acetic acid in prisms melting at 217°. The tetra-acetyl derivative of the former, $C_{14}H_6O_4Br_4Ac_4$, crystallises in rhombic plates melting at 231°, whereas the corresponding *derivative* of the *iso*-compound forms acicular crystals melting at 191°. Both are very readily hydrolysed, forming the corresponding diacetates. A mixture of these tetra-acetyl derivatives is also obtained when the quinone is boiled with acetic anhydride until all the solid has dissolved; on cooling the product of the reaction, the acetyl compound, which melts at 231°, separates first.

Tetrabromodi-p-*hydroxy-hydro-* and iso*hydro-benzoins* are obtained when the respective diacetates are hydrolysed by sodium hydroxide; the normal compound, probably in the form of an anhydride, $C_{28}H_{18}O_7Br_8$, crystallises in long prisms which begin to decompose at 250° and melt, with evolution of gas, at 280°, and is converted, on treatment with acetic anhydride and sodium acetate, into the tetra-acetyl derivative (m. p. 231°) already described; the *iso*-compound, $C_{14}H_{10}O_4Br_4$, is not definitely crystalline and melts and decomposes at 270°; by acetic anhydride, it is converted into a mixture of the two tetra-acetyl derivatives (m. p. 231° and 191° respectively).

On boiling the ψ-hexabromide with a large excess of acetic anhydride, *tetrabromodi*-p-*acetoxystilbene dibromide*, $C_2H_2Br_2(C_6H_2Br_2\cdot OAc)_2$, is formed together with the diacetate of tetrabromodihydroxystilbene and the tetra-acetate of tetrabromodihydroxyhydrobenzoin; it crystallises in elongated plates melting and decomposing at 261°, and can also be prepared by the action of bromine on tetrabromodihydroxystilbene diacetate. K. J. P. O.

Action of Chlorine on Di-*p*-hydroxystilbene and Di-*p*-aminostilbene. Theodor Zincke and K. Fries (*Annalen*, 1902, **325**, 44—67. Compare preceding abstract).—On chlorinating the hydro-

chloride of diaminostilbene, a mixture of two *keto-chlorides* is obtained; the one, $C_{14}H_5O_2Cl_{11}$, forms very insoluble crystals melting and decomposing at 217°; the other, $C_{14}H_4O_2Cl_{14}$, is a more soluble, amorphous powder which melts and decomposes at 150°. If diaminostilbene is chlorinated in the absence of hydrochloric acid, there is present after a few minutes a substance which is probably the *iminomethylenequinone*, $C_2H_2(:C_6H_4:NH)_2$; this forms a brown, amorphous, insoluble powder, and, when boiled with methyl alcohol, yields the *dimethyl ether* of diaminohydrobenzoin, $C_2H_2(OMe)_2(C_6H_4 \cdot NH_2)_2$, which crystallises in white leaflets melting at 203—204° and furnishes a *hydrochloride* crystallising in yellow leaflets. On reducing with stannous chloride either of the keto-chlorides above mentioned, or the mixture formed by chlorinating diaminostilbene, tetrachlorodi-*p*-hydroxystilbene is obtained, tetrachlorostilbenequinone being formed as an intermediate product. The tetrachlorodi-*p*-hydroxystilbene is more readily prepared from dihydroxystilbene, which is converted by chlorination into the tetrachloro-ψ-dichloride, and the latter then reduced by tin and hydrochloric acid. *Tetrachlorodi*-p-*hydroxystilbene*,

$$C_2H_2(C_6H_2Cl_2 \cdot OH)_2,$$

crystallises in long, white needles melting at 237—238° and is soluble in alkalis; its *diacetyl* derivative crystallises in needles melting at 246°. *Tetrachlorodihydroxydibenzyl*, $C_2H_4(C_6H_2Cl_2 \cdot OH)_2$, prepared by reducing the dihydroxystilbene with sodium amalgam, crystallises in needles melting at 160°; its *diacetyl* derivative forms needles melting at 159°.

Tetrachlorodi-p-*hydroxydibenzyl* ψ-*dichloride* (*tetrachlorodi*-p-*hydroxystilbene dichloride*),

$$C_2H_2Cl_2\left(CH{<}{}^{CH:CCl}_{CH:CCl}{>}CO\right)_2 \quad \text{or} \quad C_2H_2Cl_2(C_6H_2Cl_2 \cdot OH)_2,$$

can be prepared either by chlorinating dihydroxystilbene or its tetrachloro-derivative in acetic acid solution; it crystallises in needles melting and decomposing at 240°, and by the prolonged action of chlorine is converted into *keto-chlorides*; one of these, $C_{14}H_6O_2Cl_{12}$, forms crystals melting at 223—224°. *Tetrachlorodi*-p-*hydroxydibenzyl* ψ-*dibromide* (*tetrachlorodi*-p-*hydroxystilbene dibromide*), $C_{14}H_8O_2Cl_4Br_2$, prepared by the action of bromine on the tetrachlorodihydroxystilbene, crystallises in white needles melting and decomposing at 248°.

Tetrachlorostilbenequinone (*tetrachlorodibenzylidenequinone*),

$$C_2H_2\left(:C{<}{}^{CH:CCl}_{CH:CCl}{>}CO\right)_2,$$

is obtained by the oxidation of tetrachlorodihydroxystilbene (with nitric acid or bromine and alcohol), or preferably by effecting the elimination of halogen from the ψ-halogen compounds just described by boiling with acetone; it resembles red phosphorus very closely in appearance, crystallises from nitrobenzene in steel-blue needles, and, when heated to 320°, passes into an insoluble, yellow compound; with alkalis, the quinone forms green additive products.

Tetrachlorodi-p-*hydroxy-hydro*- and iso*hydro-benzoin dimethyl ethers*, $C_2H_2(OMe)_2(C_6H_2Cl_2 \cdot OH)_2$, are both formed by boiling the quinone with methyl alcohol and a few drops of sulphuric acid, and are separated by fractional crystallisation from acetic acid, in which the normal

compound is less soluble; the latter crystallises in large prisms melting at 242°; its *diacetyl* derivative crystallises in monoclinic plates melting at 164°; the iso*ether*, which is formed only in small quantity, crystallises in quadratic plates melting at 168°. The normal ether is also obtained by heating tetrachlorodihydroxystilbene with methyl alcohol and adding bromine (1 mol. to each mol. of the stilbene); at the same time, a *monomethyl* ether,

$$OH\cdot C_6H_2Cl_2\cdot CO\cdot CH(OMe)\cdot C_6H_2Cl_2\cdot OH,$$

is formed, which crystallises in small needles melting at 155—156°; its *diacetyl* derivative melts at 128—130°.

The corresponding *ethyl* ether is prepared in an exactly similar manner from tetrachlorodihydroxystilbene, ethyl alcohol being substituted for methyl alcohol; the ether crystallises in needles melting at 183—184°; its *diacetyl* derivative forms small needles melting at 139°.

Tetrachlorodihydroxy-hydro- and iso*hydro-benzoin diacetates*,

$$C_2H_2(OAc)_2(C_6H_2Cl_2\cdot OH)_2,$$

are obtained by boiling the quinone with acetic anhydride and sodium acetate; the normal compound, which separates first, forms long prisms containing acetic acid and melting at 220°, and is very easily hydrolysed by alkalis; the *iso*-compound forms small, cubic crystals melting at 202°; the *diacetyl* compound of the last-mentioned substance crystallises in prisms melting at 180°; the *diacetyl* derivative of the normal compound is obtained not only by the direct acetylation of the hydrobenzoin, but also by treating the quinone with acetic anhydride in the presence of sulphuric acid; it crystallises in well-formed prisms melting at 173° and assumes a deep blue colour with sulphuric acid.

Amines attack the quinone readily, but the course of the reaction is not the same in all cases; methylaniline, dimethylaniline and *o*-phenylenediamine reduce the quinone to tetrachlorodihydroxystilbene; methylamine and dimethylamine form indefinite, amorphous, additive compounds. The quinone is slowly dissolved by aniline, forming a *dianilino*-derivative, $C_2H_2(NHPh)_2(C_6H_2Cl_2\cdot OH)_2$, which is a white powder sintering at 130° and melting and decomposing at 158°.

When boiled with acetic anhydride, the ψ-hexachloride yields mainly tetrachlorodihydroxystilbene diacetate, together with the tetra-acetyl derivative of tetrachlorodihydroxyhydrobenzoin. If a small quantity of acetyl chloride is added to the mixture of ψ-hexachloride and acetic anhydride, *tetrachlorodi*-p-*acetoxystilbene dichloride*,

$$C_2H_2Cl_2(C_6H_2Cl_2\cdot OAc)_2,$$

is the main product; it crystallises in small, thick, insoluble plates. The ψ-tetrachloro-dibromide, on similar treatment, gives *tetrachlorodi*-p-*acetoxystilbene dibromide*, which crystallises in colourless plates melting at 218°, together with considerable amounts of the diacetate of tetrachlorodi-*p*-hydroxystilbene (m. p. 246). K. J. P. O.

Action of Chlorine on Di-*p*-aminotolane and Tetrachlorodi-*p*-hydroxytolane. THEODOR ZINCKE and K. FRIES (*Annalen*, 1902, **325**, 67—92. Compare preceding abstracts).—The di-*p*-aminotolane, $NH_2\cdot C_6H_4\cdot C\vdots C\cdot C_6H_4\cdot NH_2$, which forms the starting point of this investigation, is prepared from dinitrotolane; it crystallises in pale

yellow needles melting at 235° and is somewhat unstable; the *hydrochloride*, $C_{24}H_{16}(NH_2)_2,2HCl$, forms small crystals; the *sulphate* is slightly soluble; the *diacetyl* derivative crystallises in white needles melting above 270°, and becomes blue when exposed to light. When diaminotolane is boiled with dilute acids or alcohol, it is converted into diaminodeoxybenzoin; if hydrochloric acid is used, the *hydrochloride* of this base separates in crystals; the *base*, $NH_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot C_6H_4\cdot NH_2$, crystallises in flattened needles melting at 145°; the *sulphate* forms small needles; the *monoacetyl* derivative is obtained as needles melting at 198—205° when diaminotolane is boiled with acetic acid, but the *diacetyl* derivative, prepared by the action of acetic anhydride on the base, crystallises in needles melting at 272°.

Di-p-*hydroxydeoxybenzoin*, $OH\cdot C_6H_4\cdot CO\cdot CH_2\cdot C_6H_4\cdot OH$, is prepared from the sulphate of diaminodeoxybenzoin or diaminotolane by diazotisation and subsequent boiling of the product with water; the compound crystallises in colourless needles melting at 214—215°; its *diacetyl* derivative crystallises in needles melting at 125°.

Tetrachlorodi-p-*hydroxytolane*, $C_2H_2\left(C{<}^{CH\cdot CCl}_{CH:CCl}{>}C\cdot OH\right)_2$, is prepared by boiling the diacetate of tetrachlorodihydroxystilbene dibromide with alkalis; at the same time, a small quantity of tetrachlorodihydroxybenzil is formed; the tolane derivative crystallises in long needles melting at 226°; its *diacetyl* derivative forms leaflets melting at 234°. *Tetrachlorodi*-p-*hydroxytolane dichloride* (*hexachlorodi*-p-*hydroxystilbene*), $C_2Cl_2(C_6H_2Cl_2\cdot OH)_2$, is prepared by reducing with either tin and hydrochloric acid in acetic acid solution, or zinc and hydrochloric acid in ethereal solution, the keto-chlorides which are obtained when diaminotolane is chlorinated; it crystallises in elongated needles melting at 248°; its *diacetyl* derivative forms long needles melting at 182°; on oxidation, it is converted into the hexachlorostilbenequinone previously described; tetrachlorodi-*p*-hydroxydibenzyl is obtained on reduction with sodium amalgam.

Tetrachlorodi-p-*hydroxydibenzyl ψ-tetrachloride* (*tetrachlorodi*-p-*hydroxytolane tetrachloride*),

$$C_2Cl_4\left(CH{<}^{CH:CCl}_{CH:CCl}{>}CO\right) \text{ or } C_2Cl_4\left(C{<}^{CH\cdot CCl}_{CH:CCl}{>}C\cdot OH\right)_2,$$

is obtained by chlorinating tetrachlorodihydroxytolane or tetrachlorodihydroxytolane dichloride; in both cases, hexachlorostilbenequinone is also produced; for purposes of purification, it is best to convert the whole product into this quinone and then regenerate the ψ-octochloride by treatment with hydrogen chloride in acetic acid solution; this compound crystallises with 2 mols. of acetic acid and melts and decomposes at 222°; when free from acetic acid, it crystallises in monoclinic forms; it readily loses 2 mols. of hydrogen chloride, yielding hexachlorostilbenequinone, and, on reduction, is converted into tetrachlorodihydroxytolane dichloride. By the prolonged action of chlorine, the ψ-octochloride is converted into a mixture of two isomeric *keto-chlorides*, $C_{14}H_5O_2Cl_{13}$, which are separated by extraction with acetic acid containing hydrogen chloride, and are probably identical with the keto-chlorides prepared from diaminotolane; the insoluble portion is a crystalline powder melting at

258°; the soluble portion forms small crystals melting at 212°; on reduction, both give tetrachlorodihydroxytolane dichloride.

Tetrachlorotolanequinone dichloride (*hexachlorobenzylidenequinone*), $C_2Cl_2\left(:C<\begin{smallmatrix}CH:CCl\\CH:CCl\end{smallmatrix}>CO\right)_2$, can be prepared by oxidising tetrachlorodihydroxytolane dichloride, or, preferably, from the ψ-octochloride, from which 2 mols. of hydrogen chloride are eliminated by boiling with alcohol and sodium acetate; the quinone crystallises in red needles melting at 249°, is readily converted into the ψ-octochloride by the addition of 2 mols. of hydrogen chloride, and is reduced to tetrachlorodihydroxytolane dichloride.

*Tetrachlorodi-*p*-acetoxytolane tetrachloride*, $C_2Cl_2(C_6H_2Cl_2{\cdot}OAc)_2$, is formed when the ψ-octochloride is boiled with acetic anhydride; it forms small crystals melting at 176—177°. By heating with water, methyl alcohol, or acetic acid, the ψ-octochloride is converted into *tetrachlorodi-*p*-hydroxybenzil*, $C_2O_2(C_6H_2Cl_2{\cdot}OH)_2$; this compound crystallises in small, yellow needles which do not melt at 300° and can be sublimed in white flakes; its *diacetyl* derivative can be obtained either by direct acetylation or from tetrachlorotolanequinone dichloride; it forms yellow plates melting at 165°. With *o*-phenylenediamine, the benzil yields a *quinoxaline*, $C_6H_4<\begin{smallmatrix}N:C{\cdot}C_6H_2Cl_2{\cdot}OH\\ \vert \\ N:C{\cdot}C_6H_2Cl_2{\cdot}OH\end{smallmatrix}$, which forms small, rhombic crystals melting at 256—257° and dissolves in sulphuric acid, without decomposition, to a red solution.

*Tetrabromodi-*p*-hydroxybenzil*, $C_2O_2(C_6H_2Br_2{\cdot}OH)_2$, is produced in many of the transformations of tetrabromodi-*p*-hydroxystilbene (see preceding abstracts) and is most simply prepared by treatment of di-*p*-hydroxydeoxybenzoin with bromine in the presence of acetic acid; it crystallises in small needles which do not change at 270°; its *diacetyl* derivative crystallises in yellow plates melting at 191°; the *quinoxaline*, $C_{20}H_{10}O_2N_2Br_4$, derived from it, crystallises in small, yellow plates melting at 240°.

Tetrachlorodi-*p*-hydroxytolane dichloride is converted by bleaching powder into *di-*p*-ketohexachlorotolane dichloride*,

$$C_2Cl_2\left(C<\begin{smallmatrix}CH:CCl\\CH{\cdot}CCl_2\end{smallmatrix}>CO\right)_2,$$

which forms small, compact prisms melting at 185°, is darkened by exposure to light, liberates iodine from potassium iodide, and is reconverted into the tolane dichloride on reduction. K. J. P. O.

Synthesis of Acetylmethylmorpholquinone. ROBERT PSCHORR and H. VOGTHERR (*Ber.*, 1902, **35**, 4412—4415. Compare Abstr., 1900, i, 487).—The constitution of methylmorphol as 4-hydroxy-3-methoxyphenanthrene is proved by the synthesis of a derivative of this substance from phenylacetic acid and *vic.*-*o*-nitro*iso*vanillin (this vol., i, 167 and 175).

For this purpose, *α-phenyl-2-nitro-3-acetoxy-4-methoxycinnamic acid*, $OMe{\cdot}C<\begin{smallmatrix}CH\text{———}CH\\C(OAc):C(NO_2)\end{smallmatrix}>C{\cdot}CH:CPh{\cdot}CO_2H$, which crystallises in needles melting at 201° (corr.), is first prepared by Perkin's reaction.

This is converted by reduction into *a-phenyl-2-amino-3-hydroxy-4-methoxy-cinnamic acid*, which crystallises in yellow needles melting at 180° (corr.). The corresponding *diazo*-compound, $C_{16}H_{14}O_5N_2$, crystallises in red needles which decompose at 150° when rapidly heated. This substance decomposes in boiling alkaline solution forming *4-hydroxy-3-methoxy-phenanthrene-9-carboxylic acid*, which crystallises in almost colourless needles melting at 264° (corr.). The corresponding *acetyl* compound is more readily obtained pure, and crystallises in needles melting at 244° (corr.). On oxidation, it is converted into 4-acetoxy-3-methoxy-phenanthraquinone, $\begin{array}{l} CH{=\!=\!=\!=}CH\cdot C\cdot CO\cdot CO \\ \vert \qquad\qquad\qquad\;\; \Vert \\ C(OMe){:}C(OAc)\cdot C{-\!-\!-\!-} \end{array}\!\!>C_6H_4$, which is identical with the acetylmethylmorpholquinone prepared by Vongerichten from methylmorphol. A. H.

Mechanism of the Dehydration of Menthol by Organic Acids. I. ZELIKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 721—729).—The author has examined succinic, tartaric, citric, phthalic, terephthalic, and camphoric acids to see whether these are capable, like oxalic acid, of removing water from the menthol molecule. All these acids, except tartaric acid, possess this property in varying degree, and are also capable of converting capryl alcohol into the corresponding unsaturated hydrocarbon. The temperatures at which menthol is acted on are different for the different acids, being 200—220° for succinic acid, 160—180° for citric acid, 240—270° for phthalic acid, 270° for terephthalic acid, and 280° for camphoric acid, the yields of menthene obtained with the last two acids being about 50 and 40 per cent. respectively of the amount of menthol taken.

When menthol and oxalic acid are heated together for some hours at 110—115°, they give rise to (1) normal menthyl oxalate and (2) an *acid ester*, $C_{12}H_{20}O_4$, which is a viscous liquid, readily decomposing into oxalic acid and the normal ester; when heated with excess of oxalic acid, this compound yields the theoretical amount of menthene, whilst the normal ester, under these conditions, gives smaller quantities of the hydrocarbon.

In the reactions with succinic and phthalic acids, the corresponding acid esters are also formed.

With citric acid, *menthyl dihydrogen citrate*, $C_{16}H_{26}O_7$, is obtained as a stable, glassy mass which yields menthene when heated with excess of citric acid.

Menthyl hydrogen camphorate, $C_{20}H_{34}O_4$, is a glassy mass which, when heated with excess of camphoric acid, yields menthene.

In the case of tartaric acid, no menthene is obtained from menthol, because the acid decomposes before the acid ester, so that the latter yields no free acid. With the other acids named, the production of menthene is due to the decomposition by heat of the acid ester into menthene and the normal ester; with the excess of acid, the latter again gives the acid ester, which then decomposes, these actions going on until the whole of the menthol is converted into menthene. T. H. P

Synthesis of Menthane- and Camphane-carboxylic Acids. NICOLAI ZELINSKY (*Ber.*, 1902, **35**, 4415—4419. Compare Abstr., 1902, i, 670, and Houben and Kesselkaul, this vol., i, 42).—When menthyl bromide, obtained by the action of phosphorus pentabromide on menthol, is distilled, it yields three fractions boiling at 96—98°, 98—101°, and 101—103° under 14 mm. pressure. All three fractions possess feeble rotatory powers; the two lower are dextro-, and the highest and largest fraction lævo-rotatory.

Menthanecarboxylic acid, $CH_2<\begin{matrix}CHMe-CH_2\\CH_2\cdot CHPr^\beta\end{matrix}>CH\cdot CO_2H$, obtained by the action of magnesium and carbon dioxide on an ethereal solution of the fraction boiling at 101—103°, crystallises from methyl alcohol in colourless needles, melts at 65°, distils at 167° under 21 mm. pressure, is readily soluble in most organic solvents, and is lævorotatory. Its *calcium* salt is less soluble in hot water than in cold, the *zinc* salt is sparingly, and the *barium* salt readily, soluble in water, the *lead* salt is amorphous and dissolves in ether.

Bornyl iodide, obtained by the action of fuming hydriodic acid on borneol at 100° (Kachler, *Annalen*, 1879, **197**, 99), distils at 116—117° under 15—16 mm. pressure and has a sp. gr. 1·4416 at 21°/10°, n 1·5384 at 27°; it appears to be a mixture identical with that described by Wagner and Brickner (Abstr., 1900, i, 46). On treatment with magnesium and carbon dioxide, it yields *camphanecarboxylic acid* melting at 69—71°.

In the action between pinene hydriodide, magnesium and carbon dioxide, a considerable quantity of a liquid *hydrocarbon*, $C_{10}H_{18}$, is produced, probably a liquid modification of camphane. It boils at 157—159°, has a sp. gr. 0·8413 at 21°/4°, n 1·4548 at 21°, and is optically active. Small amounts of solid camphane are also formed.

J. J. S.

Cadinine Dihydrochloride and Dihydrobromide and a Dextrorotatory Cadinine. ÉMILIEN GRIMAL (*Compt. rend.*, 1902, **135**, 1057—1059).—The cadinine, $C_{15}H_{24}$, obtained from the oil from the wood of *Cedrus atlantica*, is crystalline, melts at 117—118°, and boils at 273—275°, has a sp. gr. 0·9224 at 15°, n_D 1 5107 at 20°, $[\alpha]_D$ +48°7′ at 20°; molecular weight in benzene 202·8. The *dihydrochloride* melts at 117—118°, and has $[\alpha]_D$ +8°55′ in chloroform and +25°40′ in ethyl acetate at 20°. When the hydrochloride is treated with sodium acetate and acetic acid, cadinine is regenerated, and has a sp. gr. 0·9212 at 15°, n_D 1·5094, and $[\alpha]_D$ +47°55′ at 20°.

C. H. B.

Ethereal Oils. SCHIMMEL & CO. (*Chem. Centr.*, 1902, ii, 1207—1208; from *Geschäftsber*, October, 1902. Compare Abstr., 1902, i, 550).—According to Nakazo Sugiyama, "camphor crude oil" is prepared by distilling shavings of camphor wood with water and removing the camphor which separates from the oil on cooling. When this oil is fractionated, it yields "camphor white oil," boiling at about 150—195°, a further quantity of camphor and "camphor red oil" boiling at about 225—270°. The white oil has a sp. gr. 0·87—0·91 and consists chiefly

of pinene, phellandrene, cineol, and dipentene. The red oil has a brownish colour, a sp. gr. 1·0—1·035, and is composed mainly of safrole together with small quantities of camphor and eugenol; the safrole may be isolated by strongly cooling the fraction boiling at 225—240°. Schimmel & Co. have found that the constituents of camphor oil which are soluble in alkalis contain not only eugenol but also carvacrol and possibly another phenol, hexoic acid, boiling at 113—114° under 4 mm. pressure, and an acid, $C_9H_{16}O_2$.

The oil of *Camphorosma Monspeliaca* (*Chenopodiaceæ*, S. France), prepared by Cassan (*Etude sur le Camph. Monsp.*, *Montpellier*, 1901) by distillation and extraction with ether, is a greenish-yellow liquid, has an odour similar to that of bitter almonds, solidifies at +4°, has a sp. gr. 0·97 at 17°, and n_D 1·3724 at 15°. When the plant is treated with potassium hydroxide solution, propylamine is formed.

Bergamot oil (Gulli, *Chemist and Druggist*, 1902, **60**, 995) has a sp. gr. 0·870—0·873, rotatory power $\alpha + 25°$ to $+26°$, and contains 32—34 per cent. of esters calculated as linalyl acetate. Methyl anthranilate is also present in the oil.

Lemon oil contains citronellal, phellandrene, methylheptenone, terpineol, and probably also *l*-camphene (compare Burgess and Child, *Chemist and Druggist*, 1902, **60**, 812). Terpineol melts at 35° and forms a phenylurethane which melts at 110°.

Liquid musk oil, prepared by removing the fatty acids, which consist probably of palmitic acid, dissolves in 5—6 parts of 80 per cent. alcohol, has a sp. gr. 0·909, $\alpha + 1°10'$, an acid number 2·4, and an ester number 180·5.

The average of 11 samples of Neroli oil distilled from the harvest of 1902 by Jean Grass, in Cannes, had a sp. gr. 0·8733 at 15°, α_D +3°22′ at 20°, and a saponification number 45. The oil dissolved in 2 volumes of 80 per cent. alcohol, but further addition of alcohol caused the solution to become turbid. When French Neroli oil was fractionated under diminished pressure, the first fractions boiling at 160—180° under the ordinary pressure did not give the pyrrole reaction (compare Erdmann, Abstr., 1899, i, 621), but contained *l*-pinene, *l*-camphene, and dipentene; a small quantity of an aldehyde which had the odour of decoic aldehyde was also isolated. When the fraction boiling at 82—97° under 8 mm. pressure was hydrolysed, phenylacetic acid was formed, whilst the residue from the distillation, when similarly treated, yielded benzoic acid; both these acids are probably combined with benzyl alcohol or phenylmethylcarbinol; the latter being obtained by hydrolysing the fraction boiling at 210—220°. An alcohol, $C_{10}H_{18}O$, found in the fractions boiling at 76—79° and at 88—97° under 8 mm. pressure, which is probably *l*-linalool, boils at 196—199° and has a sp. gr. 0·870—0·871 and α about −8°20′, and forms a phenylurethane which melts at 65° (compare below, petit grain oil). From the fractions boiling at 90—114° under 7 mm. pressure, terpineol, melting at 35°, was isolated. Although Neroli oil has the odour of indole, the presence of this compound could not be directly detected (compare Hesse, Abstr., 1900, i, 48).

Petit grain oil (Paraguay) contains furfuraldehyde, *l*-pinene (?), *l*-camphene (?), dipentene, an alcohol, $C_{10}H_{18}O$, which is probably linalool,

and forms a phenylurethane melting at 65°, *d*-terpineol melting at 35°, geraniol, geranyl acetate, and traces of a basic compound. The first fractions of the oil give the pyrrole reaction. Linalyl phenylurethane, melting at 65—66°, may also be prepared from the *l*-linalool of oil of linalool, and from the *d*-linalool of coriander oil, hence this substance probably affords a good test for the presence of linalool in ethereal oils. The oil, which is regenerated by boiling the urethane with alcoholic potassium hydroxide solution, has all the properties of linalool. Geraniol also reacts with phenylcarbimide, but a solid urethane could not be isolated.

The oil prepared from *Pseudocymopterus anisatus* has the odour of aniseed, does not solidify, and has a sp. gr. 0·978 at 20°.

It is said that Bulgarian oil of roses is sometimes adulterated with a mixture of antipyrine and salol in order to raise its point of solidification.

Cinnamon leaf oil contains terpenes and *l*-linalool. The oil from *Bystropagon origanifolius* distils between 162° and 234°, has a sp. gr. 0·9248 at 15°, $\alpha + 2°57'$, n_D 1·48229, and a saponification number 11·1; it consists mainly of pulegone and menthone, together with a small quantity of *l*-limonene. The acetyl derivative has a saponification number 53·83.

The oil from the leaves of the mandarin tree has an odour similar to that of Neroli oil, and a blue fluorescence; it dissolves in 6—6·5 parts of 80 per cent. alcohol, has a sp. gr. 1·0142 at 15°, $\alpha + 7°46'$, and an ester number 216. E. W. W.

Ethereal Oils. HEINRICH HAENSEL (*Chem. Centr.*, 1902, ii, 1208; from *Pharm. Zeit.*, **47**, 818—819).—The oil prepared from the buds of the beech is a green liquid with a pleasant odour, solidifies at 4·5°, has a sp. gr. 0·9592 at 20°, rotatory power $-6°52'$, and is readily soluble in organic solvents with the exception of glacial acetic acid and carbon disulphide.

The oil from dammar wood is golden-yellow and has the odour of the wood and a bitter taste; it dissolves in 80 parts of 90 per cent. alcohol, and has a sp. gr. 0·9352 at 21°. Sixty per cent. of the oil distils below 240°. The oil prepared from *Genista tinctoria* is solid at the ordinary temperature, melts at 36°, is insoluble in alcohol, and has a sp. gr. 0·8980 at 33°. E. W. W.

Occurrence of Naphthalene in Ethereal Oils. HUGO VON SODEN and WILHELM ROJAHN (*Chem. Centr.*, 1902, ii, 1117; from *Pharm. Zeit.*, 1902, **47**, 779).—The presence of naphthalene has been detected in an oil of cloves and in an ethereal oil of storax bark. The hydrocarbons contained in the former oil consist mainly of caryophyllene. E. W. W.

Essential Oil of Vetiver. PAUL GENVRESSE and G. LANGLOIS (*Compt. rend.*, 1902, **135**, 1059—1061. Compare Theulier, Abstr., 1901, i, 397).—Essential oil of vetiver from Bourbon and Grasse has been examined. Its composition, specific gravity, and rotatory power vary; it contains a sesquiterpene, a sesquiterpene alcohol, the ester

which gives it its odour. *Vetivene*, $C_{15}H_{24}$, is a colourless, mobile, almost odourless liquid; it boils at 262—263° under 740 mm. pressure and at 135° under 15 mm. pressure, has a sp. gr. 0·932 at 20°, and $[\alpha]_D$ + 18°19′ at 15°. Vetivene absorbs four atomic proportions of bromine without any liberation of hydrogen bromide. *Vetivenol*, $C_{15}H_{26}O$, is a viscous, pale yellow, odourless liquid of sp. gr. 1·011 at 20°; it boils at 169—170° under 15 mm. pressure and has $[\alpha]_D$ + 53°43′ at 20°. With acetic acid, it yields an acetate, and when dehydrated it yields vetivene. The acid contained in the essence seems to have the composition $C_{15}H_{22}O_4H_2$. C. H. B.

Matico Oil. Emil Fromm and Konrad van Emster (*Ber.*, 1902, **35**, 4347—4362).—Matico oil is prepared from several species of plants and has therefore a variable composition. The sample examined was a dark brown oil with a faint odour of cedar wood, had a sp. gr. 1·123 at 15°, did not solidify either before or after fractionation, and contained no asarone or matico-camphor. The chief constituent, forming at least 70 per cent. of the oil, is *matico ether*, $C_{14}H_{18}O_4$, a substance which was obtained as a pale yellow oil of sp. gr. 1·136 at 17° with slight fluorescence, only slightly volatile with steam, and boiling at 282—285°; it darkens in colour when kept, but is decolorised by sunlight, does not dissolve in alkalis, has a zero saponification-number, does not form a benzoate, oxime, hydrazone, or bisulphite compound, and does not reduce silver oxide, but contains two methoxy-groups.

Matico-aldehyde, $C_7H_3O_2(OMe)_2 \cdot CHO$, prepared by oxidising the ether with 5 per cent. potassium permanganate, forms an oxime, hydrazone, and bisulphite compound, reduces ammoniacal silver oxide, and contains two methoxy-groups; it crystallises from 50 per cent. alcohol in white needles, distils readily in a current of steam, and melts at 88°; the *oxime* crystallises from water and melts at 154°; the *phenylhydrazone* crystallises from alcohol in colourless tablets and melts at 163°.

Maticoic acid, $C_7H_3O_2(OMe)_2 \cdot CO_2H$, which is also formed in the oxidation, crystallises from hot water in white needles and melts at 138°; the *copper* salt forms a dark green, insoluble precipitate; the *lead* salt is a white powder somewhat soluble in water; the *barium* salt separates in cauliflower-like crystal aggregates.

Homomaticoic acid, $C_{11}H_{12}O_6$, probably $C_7H_3O_2(OMe)_2 \cdot CH_2 \cdot CO_2H$, an intermediate product of oxidation, was isolated by acting on the ether with cold 2 per cent. permanganate; it crystallises from hot water in needles and melts at 96°; the crystalline *barium* salt, $(C_{11}H_{11}O_6)_2Ba,H_2O$, was analysed.

The *bromide*, $C_{11}H_{13}O_3Br_3$, prepared by the action of an excess of bromine on an ethereal solution of the ether, crystallises in needles from light petroleum or from alcohol and melts at 116°; the loss of three carbon atoms in bromination suggests that it is a compound similar to maticoic acid, but the elimination of an oxygen atom is less easy to account for.

It is suggested that matico ether has the formula

$$CH_2{<}^{O}_{O}{>}C_6H(OMe)_2{\cdot}CH_2{\cdot}CH_2{:}CHEt \text{ or}$$

$$CH_2{<}^{O}_{O}{>}C_6H(OMe)_2{\cdot}CH_2{\cdot}CH_2{:}CMe_2\ [(OMe)_2{:}CH_2O_2 = 2:3:5:6], \text{but}$$

direct evidence of the presence of a methylene-ether group could not be obtained. T. M. L.

Essential Oil of Orange Blossoms. II. ALBERT HESSE and OTTO ZEITSCHEL (*J. pr. Chem.*, 1902, [ii], **66**, 481—516. Compare Abstr., 1901, i, 733).—Contrary to Tiemann and Semmler's statement (Abstr., 1894, i, 83), oil of neroli contains not more than 16—17 per cent. of linalyl acetate. An average sample of oil of neroli has a sp. gr. 0·870—0·875 at 15°, α_D +2·5° to +6°, and has the composition: pinene, camphene, dipentene, and paraffin, $C_{27}H_{56}$, 35; *l*-linalool, 30; *l*-linalyl acetate, 7; *d*-terpineol, 2; geraniol and nerol, 4; geranyl acetate and neryl acetate, 4; *d*-nerolidol, 6; methyl anthranilate, 0·6; indole, less than 0·1; acetic and palmitic acids, 0·1; decoic aldehyde (?) and esters of phenylacetic and benzoic (?) acids, 11·2 per cent.

The paraffin, $C_{27}H_{56}$, crystallises in white, silky leaflets and melts at 54°. It is probably identical with nerolicamphor or aurade.

Nerol, $C_{10}H_{18}O$, is an oil which boils at 225—227° under 765 mm. pressure, has a sp. gr. 0·886, and is distinguished from geraniol by its odour of roses and by its inactivity towards calcium chloride. *Neryl-diphenylurethane*, $NPh_2{\cdot}CO_2{\cdot}C_{10}H_{17}$, formed from nerol by the action of diphenylcarbamide chloride in presence of pyridine (compare Erdmann and Huth, Abstr., 1898, i, 35), crystallises in delicate needles and melts at 73—75°.

Nerolidol is an oil which boils at 128—129° under 6 mm., at 164—165° under 25 mm., and at 276—277° under atmospheric pressure; it has α_D +13·32°, a sp. gr. 0·880, and has only a slight odour.

That part of the oil of orange blossoms which distils with water has a sp. gr. 0·945 at 15°, α_D +2·30°, and contains methyl anthranilate, geraniol, nerol, indole, phenylmethylcarbinol, and phenylacetic acid. The oil obtained from orange pomade gives similar results. G. Y.

Oil of Verbena from Grasse. EUGÈNE THEULIER (*Bull. Soc. chim.*, 1902, [iii], **27**, 1113—1117).—The fresh leaves of *Verbena triphylla*, when distilled with steam, yield 0·72 per cent. of oil; this has a bright yellow colour, an odour recalling that of lemon-grass, a sp. gr. 0·919 at 13°, and α_D −16°20′; it contains 11·29 per cent. of esters calculated as linalyl acetate and 20·8 per cent. of aldehydes, principally citral. The non-aldehydic residue has a sp. gr. 0·920 at 15° and α_D −22° [? 100 mm.], and consists chiefly of *l*-limonene, geraniol, and a sesquiterpene (compare Kerschbaum, Abstr., 1900, i, 353). T. A. H.

Chemistry of India-rubber. II. CARL D. HARRIES (*Ber.*, 1902, **35**, 4429—4431. Compare Abstr., 1902, i, 811).—Full directions for the preparation of the nitrosite *c*, $C_{20}H_{30}O_{14}N_6$ (*loc. cit.*), are given. When the nitrous fumes from white arsenic and nitric acid are dried

with phosphoric oxide and passed into a benzene solution of india-rubber, the insoluble nitrosite, $(C_{10}H_{16}O_3N_2)_x$, is obtained, and this, when left in contact with benzene and excess of nitrous acid, becomes soluble in ethyl acetate, and the solution so obtained, on further treatment with nitrous fumes dried over phosphoric oxide, and precipitation with ether, yields the nitrosite *c* decomposing at 158—162°. The nitrosite *b* previously described was formed owing to the fact that the nitrous fumes were dried over calcium chloride and thus contained chlorine and nitrosyl chloride, which acted as oxidising agents.

J. J. S.

Chemical Behaviour of Gutta-percha. Sir WILLIAM RAMSAY, Miss HARIETTE CHICK, and FRANK COLLINGRIDGE (*J. Soc. Chem. Ind.*, 1902, 21, 1367—1372).—Gutta-percha has been said to consist of a hydrocarbon, gutta, a crystalline resin, alban, and a non-crystalline portion, fluavile. The gutta is separated from the resins by dissolving in toluene and precipitating with acetone, then freed from mineral matter by dissolving in chloroform, removing undissolved matter by filtration, and precipitating with alcohol. Thus obtained, it is a white substance which oxidises extremely readily in the air. Analysis shows that its composition is approximately represented by C_5H_8 (? $C_{34}H_{54}$), but its molecular weight could not be ascertained. On dry distillation of gutta, an oil is obtained which boils at 34—38° and gives a hydrogen bromide additive compound having the formula $C_5H_{10}Br_2$. By the action of bromine on gutta, a white, amorphous powder is produced, the formula of which may be $C_{10}H_{16}Br_4$ or $C_{17}H_{27}Br_7$, and by the action of hydriodic acid a colourless oil boiling at 320—360° under 20 mm. pressure is obtained, the formula of which is $C_{27}H_{46}$. When gutta is treated with a mixture of nitric and sulphuric acids, it dissolves, and the solution deposits a yellow precipitate when poured into water; this yellow substance is soluble in sodium hydroxide solution, but insoluble in the common organic solvents. Its formula is either $C_{21}H_{31}O_{13}N_3$ or $C_{34}H_{54}O_{21}N_5$. When gutta is oxidised by atmospheric oxygen in ethereal solution, a substance is obtained which has nearly the same composition as alban (*vide ultra*); the formula established for it is $C_{17}H_{26}O$. Oxidation in toluene solution takes a different course, so that a sticky solid is formed having the formula $C_{12}H_{24}O_4$; when distilled under reduced pressure, this decomposes into carbon monoxide, carbon dioxide, methane, and a yellow oil having the formula $C_{12}H_{20}O_3$, which has the odour of peppermint.

The authors have not been able to isolate the alban ($C_{10}H_{16}O$) described by Oudemans and by Payen, but an old, highly oxidised gutta-percha, when extracted, gave results indicating that alban consists of two substances, a crystalline compound, $C_{17}H_{26}O$, and a resin having the formula $C_{17}H_{28}O$. When alban is treated with phosphorus pentachloride, it yields a crystalline compound melting at 170° which has the formula $C_{40}H_{63}O_3Cl$. In solution in acetic acid, the maximum oxidation with chromic acid appears to take place when the proportion of three atoms of oxygen to one molecule of alban is employed; the product formed has the formula $(C_8H_{13}O)_n$. During

the oxidation, acetaldehyde, acetic acid, and carbon dioxide are formed; these were detected by carrying out the reaction in chloroform solution. Substances of melting points 120—130°, 133°, 120—125°, and 144° are obtained when varying quantities of chromic acid are employed. J. McC.

Acocantherin: African Arrow Poisons. Edwin S. Faust (*Chem. Centr.*, 1902, ii, 1217; from *Arch. exp. Path. Pharm.*, 48, 272—281).—From the "Shushi" arrow poison, which is prepared from *Acocanthera abyssinica*, a poisonous glucoside, *acocantherin*, $C_{32}H_{50}O_{12}$, has been isolated; it is precipitated in yellow flakes on addition of ether to its alcoholic solution. It is extremely hygroscopic, has a very bitter taste, softens at about 130°, decomposes at 220°, is optically inactive, readily soluble in alcohol or water, but insoluble in ether, chloroform, benzene, acetone, light petroleum, or ethyl acetate, and is precipitated from its aqueous solution by potassium mercuric iodide. When boiled with mineral acids, the glucoside yields rhamnose, the other component separating from the acid solution of the glucoside on warming, in the form of lamellæ which are soluble in 96 per cent. alcohol, chloroform, or acetic anhydride.

Acocantherin is a homologue of ouabain (Abstr., 1898, i, 377, 597, 677) and strophanthin, and is possibly dimethylouabain. It is probably identical with the glucoside isolated by Brieger (*Berl. klin. Woch.*, 39, No. 13) from the fruit kernels and branches of *Acocanthera abyssinica*. The physiological action of the glucoside is similar to that of the digitalis alkaloids. E. W. W.

Coca Leaves. Oswald Hesse (*J. pr. Chem.*, 1902, [ii], 66, 401—422. Compare Abstr., 1893, i, 57).—Java coca, which contains 2—2·5 per cent. of benzoyl-ψ-tropeine, resembles Truxillo coca, from which 0·8—1 per cent. of this alkaloid can be extracted.

From Java coca, the author has obtained four yellow substances: cocacitrin (Warden's cocatannic acid; Abstr., 1888, 1090), cocaflavin, cocaflavetin, and cocacetin.

Cocacitrin, $C_{28}H_{32}O_{17},3H_2O$ (Warden, $C_{17}H_{22}O_{10},2H_2O$), crystallises in thin, yellowish, six-sided prisms, loses $2H_2O$ at 120—130°, sinters at 175°, and melts at 186°, reddens litmus in alcoholic solution, and gives a deep yellow coloration with concentrated sulphuric acid and a dirty-green with ferric chloride. The *acetyl* derivative, $C_{28}H_{25}O_{17}Ac_7$, forms an almost white, brittle mass, melts at 118°, gives a brownish-red coloration with ferric chloride, and is hydrolysed by aqueous alkalis, but not by ammonia. Hydrolysis of cocacitrin with 4 per cent. sulphuric acid leads to the formation of cocacetin and *cocaose*, $C_6H_{12}O_6,H_2O$, which crystallises in glistening octahedra, melts at 89—90°, has $[\alpha]_D$ +19·8° at 15°, has a sweet taste, reduces Fehling's solution, does not undergo fermentation, and is perhaps identical with *d*-talose. The *osazone* crystallises in small, yellow needles and melts at 179—180°.

Cocacetin, $C_{16}H_{12}O_7,3H_2O$, crystallises in small, yellow needles, loses $3H_2O$ at 130°, melts at 260—265°, and is soluble in alcohol, acetone, or

glacial acetic acid. The alcoholic solution has an acid reaction and gives a dark green coloration with ferric chloride. The solutions in aqueous alkalis or ammonia are yellow and give precipitates with barium chloride, lead acetate, and silver nitrate. With sulphuric acid, cocacetin forms a derivative which crystallises in microscopic needles and is decomposed by water. The *acetyl* derivative, $C_{16}H_8O_7Ac_4$, crystallises in white prisms and melts at 180°. Fusion of cocacetin with potassium hydroxide leads to the formation of *decocacetin* (hydrodecarbonylcocacetin), $C_{15}H_{14}O_6$, which crystallises in light yellow, four-sided needles, melts at 238°, is easily soluble in hot acetone or aqueous alkali hydroxide, but insoluble in ammonia. With ferric chloride in alcoholic solution, it yields a dirty-green coloration, and forms yellow needles with concentrated sulphuric acid. When heated with potassium hydroxide and a small amount of water, decocacetin yields phloroglucinol and protocatechuic acid.

Cocaflavin, $C_{34}H_{38}O_{19},4H_2O$, crystallises in small, yellow needles or thick prisms, loses $4H_2O$ at 120—130°, and melts at 163—164°. The alcoholic solution has an acid reaction and gives a greenish-brown coloration with ferric chloride. Cocaflavin is soluble in aqueous alkali hydroxides and is reprecipitated on addition of hydrochloric acid. The solution in aqueous ammonia yields precipitates with barium, lead, and silver salts. By the action of hydriodic acid, methyl iodide is eliminated, whilst dextrose and galactose are set free under the influence of 4 per cent. sulphuric acid.

Cocaflavetin, $C_{20}H_{12}O_7(OMe)_2,3H_2O$, crystallises in greenish-yellow, flat needles or yellowish leaflets, loses $3H_2O$ at 120°, melts at 230°, is easily soluble in alcohol, acetone, or glacial acetic acid, forms yellow solutions in aqueous potassium hydroxide or concentrated sulphuric acid, and gives an intense, dark green coloration with alcoholic ferric chloride. When fused with potassium hydroxide, it forms an acid which gives a dark green coloration with ferric chloride. When treated with hydriodic acid, cocaflavetin yields *norcocaflavetin*, $C_{20}H_{12}O_7(OH)_2$, which forms yellow, crystal aggregates, melts at 270°, is easily soluble in alcohol, and gives an intense, dark green coloration with ferric chloride.

The molecular weight of cocamine agrees with the formula $C_{38}H_{46}O_8N_2$, and not with $C_{19}H_{23}O_4N$ as previously calculated (Abstr., 1893, i, 57).

*β-iso*Cocaic acid crystallises from benzene in colourless leaflets containing 1 mol. of C_6H_6, which is lost at 120°.

Protococaic acid (homococaic acid, *Pharm. J. Trans.*, [iii], 21, 1129) is now found to have the formula $C_9H_8O_2$. Proto*iso*cocaic acid (homo*iso*cocaic acid, *loc. cit.*) has probably the same formula.

G. Y.

Saponin contained in Lychnis flos cuculi. Paul Süss (*Chem. Centr.*, 1902, ii, 1264—1265; from *Pharm. Zeit.*, 47, 805—806).—*Lychnidin* (0·2 per cent.) has been isolated from *Lychnis flos cuculi* by extracting with 96 per cent. alcohol and precipitating with ether. It forms an amorphous, yellowish powder and has all the properties of a saponin. Experiments on guinea-pigs have shown

that intraperitoneal or subcutaneous injection of lychnidin causes local inflammation and acute nephritis. The continued use of small doses tends to the formation of clots in the blood. When administered by the mouth it is without effect. E. W. W.

Theory of the Dyeing Process. P. D. ZACHARIAS (*Chem. Zeit.*, 1902, **26**, 1201—1202. Compare Abstr., 1902, i, 635).—A reply to Wegscheider (Abstr., 1902, i, 635). K. J. P. O.

Degradation of Brazilin. STANISLAUS VON KOSTANECKI (*Ber.*, 1902, **35**, 4285—4288).—Polemical. Compare Gilbody and Perkin (Proc., 1899, **15**, 27, 75), and Perkin (Proc., 1902, **18**, 147; and Trans., 1902, **81**, 1048). K. J. P. O.

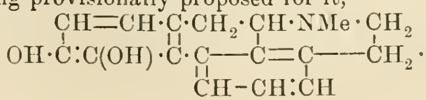
Colouring Matter of Stylophorum diphyllum and Chelidonium majus. JULIUS O. SCHLOTTERBECK (*Amer. J. Pharm.*, 1902, **74**, 584—586).—The yellow colouring matter of *Chelidonium majus* was first isolated by Probst and termed "chelidoxanthin." A colouring matter obtained by the author from *Stylophorum diphyllum* was found to be identical with "chelidoxanthin," but it is now shown that in each case the coloured substance consists of berberine.

E. G.

Alkaloids of Dicentra Cucullaria. RICHARD FISCHER and O. A. SOELL (*Pharm. Arch.*, 1902, **5**, 121—124).—An examination of this plant has shown the presence of protopine together with two other alkaloids provisionally termed *c* and *d*. Alkaloid *c*, which is almost insoluble in alcohol and only slightly soluble in chloroform, crystallises in rosettes of needles, and melts and decomposes at 230—231° (uncorr.); it rapidly turns yellow on exposure to light. Alkaloid *d* is present only in small quantity; it is fairly soluble in alcohol, forms granular crystals, and melts at 215° (uncorr.). E. G.

Alkaloids of Eschscholtzia Californica. RICHARD FISCHER and M. E. TWEEDEN (*Pharm. Arch.*, 1902, **5**, 117—121. Compare Abstr., 1901, i, 743).—Further investigation of the root of *Eschscholtzia Californica* has shown the presence of two alkaloids, *a* and *b*, in addition to those previously isolated. Alkaloid *a* is readily soluble in chloroform or hot alcohol, crystallises in colourless rosettes of thin prisms, darkens at 234°, and melts at 242—243° (uncorr.). Alkaloid *b* is sparingly soluble in alcohol but readily so in chloroform, forms granular crystals, and melts at 217° (uncorr.). E. G.

Constitution of Apomorphine. ROBERT PSCHORR, BERNHARD JAECKEL, and HERMANN FECHT (*Ber.*, 1902, **35**, 4377—4392).—Apomorphine is probably a phenanthrene-quinoline derivative, the following formula being provisionally proposed for it,



Both the oxygen atoms are present as hydroxyl groups, and diacyl and dialkyl derivatives can be prepared. The triacyl derivatives are probably formed by rupture of the reduced pyridine ring, and this ring is also destroyed by the destructive methylation of the compound, which leads finally to the formation of a dimethoxyphenanthrene-carboxylic acid. No definite inference can as yet be drawn as to the relation of apomorphine to morphine.

Apomorphine can be crystallised from ether in an atmosphere free from oxygen, and separates in colourless prisms with 1 mol. of ether, which is lost at 100°. *Dibenzoylapomorphine*, $C_{17}H_{15}N(OBz)_2$, is prepared by the Schotten-Baumann method, and crystallises in colourless prisms, melts at 156—158° (corr.), and has $[\alpha]_i$ +43·44° at 17° in chloroform solution. Apomorphine is regenerated when this compound is heated with sodium methoxide in methyl-alcoholic solution. *Dibenzoylapomorphine methiodide*, $C_{17}H_{15}N(OBz)_2,MeI$, crystallises in colourless needles melting at 229—230° (corr.). *Tribenzoylapomorphine*, $C_{17}H_{15}NBz(OBz)_2$, is obtained by the action of benzoyl chloride on apomorphine, and crystallises in very slender needles melting at 217—218° (corr.). It is optically inactive, does not yield a methiodide, and cannot be reconverted into apomorphine by hydrolysis. *Acetyldibenzoylapomorphine* is formed by the action of acetic anhydride on dibenzoylapomorphine and crystallises in colourless needles melting at 156—158° (corr.). The monoacetyl compound described by Danckwortt (*Arch. Pharm.*, 228, 572) could not be obtained. Tribenzoylapomorphine is converted by oxidation into a yellow, amorphous mass, which appears to contain *dibenzoylmorpholquinone*. Apomorphine is converted by diazomethane into a mixture of mono- and di-methyl derivatives. *Methylapomorphine* crystallises with C_2H_6O in colourless needles, decomposes when heated, has $[\alpha]_D$ +66·83° at 22°, and yields a crystalline *hydrochloride*. *Dimethylapomorphine* closely resembles the monomethyl compound. *Methylapomorphine methiodide* crystallises in colourless needles, melts at 229—230° (corr.), and has $[\alpha]_D$ +10·48° at 21°. *Benzoylmethylapomorphine* crystallises with C_2H_6O in needles melting at 85—90°. *Acetylmethylapomorphine methiodide* is prepared from methylapomorphine methiodide, and crystallises in colourless needles melting at 241—242° (corr.). *Diacetylmethylapomorphine* also crystallises in needles with C_2H_6O. *Dimethylapomorphine methiodide* crystallises in long, colourless needles, melts at 195° (corr.), and has $[\alpha]_D$ −42·03° at 21°. When dimethylapomorphine methiodide is heated with aqueous potassium hydroxide, it is converted into *dimethylapomorphimethine*, $C_6H_2(OMe)_2{:}C_2H_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, the *hydrochloride* of which crystallises in needles, melts and decomposes at 220—221° (corr.), and is optically inactive, the pyridine ring of the apomorphine having been broken. The *methiodide* crystallises in long tablets melting at 242—244° (corr.) and is decomposed by aqueous potassium hydroxide, trimethylamine being produced together with a compound free from nitrogen. This substance, which is probably 3 : 4-*dimethoxyvinylphenanthrene*, $C_{14}H_{17}(OMe)_2{\cdot}CH{:}CH_2$, crystallises in rhombic tablets melting at 80° (corr.) and yields a *picrate* melting at 128° (corr.); it unites with bromine, forming an additive com-

pound, which, by the further action of bromine, is converted into a *tetrabromo*-derivative, $C_{18}H_{14}O_2Br_4$, which crystallises in colourless needles melting at 145—147° (corr.). When heated with glacial acetic acid, it yields a *compound*, $C_{18}H_{13}O_2Br_3$, which crystallises in lustrous plates and melts at 158—159° (corr.). Dimethoxyvinylphenanthrene is converted by oxidation into 3 : 4-*dimethoxyphenanthrenecarboxylic acid*, which can be distilled under 30 mm. pressure and forms a colourless, crystalline mass. The positions of the vinyl and carboxyl groups in these compounds have not yet been ascertained.

A. H.

Aristochin, Mesotan, Helmitol, and Theocine. ARTHUR EICHENGRÜN (*Chem. Centr.*, 1902, ii, 1387; from *Pharm. Zeit.*, 47, 857—858).—Aristochin, or quinine carbonate, $(C_{20}H_{23}ON_2)_2CO_3$, is a white, tasteless powder, which melts at 189°, and is readily soluble in chloroform or alcohol, very sparingly so in ether, and insoluble in water; it combines with hydrochloric acid (1 or 2 mols.) to form soluble salts.

Mesotan, or methoxymethyl salicylate, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot OMe$, is a yellow liquid heavier than water, has a faint aromatic odour, boils at 162° under 42 mm. pressure, is soluble in all proportions in alcohol, ether, benzene, chloroform, or fatty oils, but only sparingly so in water, and gives a violet coloration with ferric chloride. At temperatures above 100°, it decomposes into salicylide, formaldehyde, methyl alcohol, and methyl salicylate, the last substance being a secondary product formed by the action of methyl alcohol on salicylide.

Helmitol is a hexamethylenetetramine compound of anhydromethylenecitric acid; it forms colourless crystals, decomposes at 163°, dissolves in about 14 parts of water forming an acid solution, is very sparingly soluble in alcohol, insoluble in ether, and is slowly attacked by dilute acids, but more readily by alkalis, with liberation of formaldehyde. Its physiological action is stronger than that of hexamethylenetetramine.

Theocine, or 1 : 3-dimethylxanthine, crystallises in colourless needles, melts at 268°, and is very sparingly soluble in cold water or alcohol, more readily so in hot water, and insoluble in ether; it is an active diuretic. The ammonium and potassium salts are readily soluble, but the sodium salt is only sparingly so. E. W. W.

Yohimbine. PAUL SIEDLER (*Chem. Centr.*, 1902, ii, 1215; from *Pharm. Zeit.*, 47, 797—798. Compare Abstr., 1899, i, 966).—The Yohimbehe bark contains at least 4 alkaloids: (1) Yohimbine, which is very sparingly soluble in ether, more so in absolute alcohol, and readily so in chloroform; (2) Yohimbenine, readily soluble in ether, absolute alcohol, or chloroform; (3) an alkaloid, readily soluble in absolute alcohol or chloroform, but only sparingly so in ether; and (4) an alkaloid which is insoluble in ether and only very sparingly soluble in alcohol or chloroform. These alkaloids may possibly be separated by means of their hydrogen sulphites or thiocyanates. *Yohimbine thiocyanate* is very sparingly soluble, separates from hot water in rectangular crystals, and melts at 233—234°; when decomposed with sodium carbonate, it yields a base

which melts at 222—223°, whilst the more soluble thiocyanate remaining in the mother liquor, when similarly treated, gives a base melting at 228—229°. E. W. W.

Action of Hydrazine on Ethyl Diacetylsuccinate. CARL BÜLOW [with E. VON KRAFFT] (*Ber.*, 1902, 35, 4311—4322).—When hydrazine hydrate interacts with alcoholic ethyl diacetylsuccinate, in addition to the compounds described by Curtius (Abstr., 1895, i, 247), there is formed a considerable quantity (about 50 per cent.) of *ethyl* 1-*amino*-2:5-*dimethylpyrrole*-3:4-*dicarboxylate*; this substance forms 70 per cent. of the product when the action takes place in glacial acetic acid solution. It crystallises from dilute alcohol, or a mixture of chloroform and light petroleum, in needles, melts at 102—103°, can be distilled under 18 mm. pressure, and gives a *benzoyl* derivative, $NHBz\cdot C_4NMe_2(CO_2Et)_2$, which crystallises from dilute alcohol, melts at 123—124°, and is also obtained by the direct action of benzoylhydrazine on ethyl diacetylsuccinate. The *dibenzoyl* derivative, $NBz_2\cdot C_4NMe_2(CO_2Et)_2$, melts at 132—133° and is hydrolysed by alcoholic potassium hydroxide to the foregoing monobenzoyl compound. The *phenylacetyl* derivative, $C_{20}H_{24}O_5N_2$, obtained either by the action of phenylacetyl chloride on the base or by the direct interaction of phenylacetic hydrazide with ethyl diacetylsuccinate, crystallises from dilute alcohol in white, lustrous needles and melts at 146—147°. 1-*Amino*-2:5 *dimethylpyrrole*, $C_6H_{10}N_2$, obtained by boiling the dicarboxylate with 10 per cent. potassium hydroxide, precipitating the acid formed with hydrochloric acid, and subsequently distilling it, crystallises from dilute alcohol, melts at 52—53°, and boils at 198—204°. When ethyl amino-2:5-dimethylpyrroledicarboxylate is decomposed with nitrous acid, a crystalline product, melting at 86—87°, is obtained, the nature of which was not established; the *acid*, derived from it by hydrolysis, melts and decomposes at 213°.

When ethyl 1-benzoylamino-2:5-dimethylpyrrole-3:4-dicarboxylate is heated with 15 per cent. hydrochloric acid for eight hours at 135—140°, it gives benzoic acid, but no other definite product; when, however, it is heated with 50 per cent. potassium hydroxide and the product acidified with acetic acid, *potassium hydrogen* 1-*benzoylamino*-2:5-*dimethylpyrrole*-3:4-*dicarboxylate*, $C_{15}H_{13}O_5N_2K,\frac{1}{2}H_2O$, is obtained as a sparingly soluble precipitate. The *dicarboxylic acid* itself crystallises from acetic acid or alcohol and melts and decomposes at 231—232°; when heated in glycerol, it loses carbon dioxide, giving 1-*benzoylamino*-2:5-*dimethylpyrrole*, which is purified by dissolving in warm dilute aqueous sodium hydroxide and precipitating with carbon dioxide; it melts at 177—179°.

1-*Phenylacetylamino*-2:5-*dimethylpyrrole*-3:4-*dicarboxylic acid*, obtained from its ethyl ester by hydrolysis with 10 per cent. potassium hydroxide for 12 hours, crystallises from alcohol and melts at 216—217°; if the heating is prolonged for five days, 1-*phenylacetylamino*-2:5-*dimethylpyrrole* is obtained; this crystallises from alcohol or a mixture of ether and light petroleum in long, stout needles, melts at 110—111° and distils at 245—265° under 26 mm. pressure.

W. A. D.

Nitriles of the Pyridine Series. Hans Meyer (*Monatsh.*, 1902, **23**, 897—906. Compare Abstr., 1902, i, 727).—2-Cyano-, 3-cyano-, and 4-cyano-pyridine are obtained by the action of thionyl chloride on the corresponding amides, the yield of the first being good, but of the other two very small.

3-Cyanopyridine forms colourless crystals, melts at 50°, boils at 240—245° (compare Fischer, *Ber.*, 1882, 15, 63), and yields an *aurichloride*, $C_6H_4N_2,HAuCl_4$, which crystallises in concentric groups of light yellow needles and melts at 196—198°.

4-*Cyanopyridine* forms colourless crystals, melts at 83°, is volatile without decomposing, and is hydrolysed by concentrated hydrochloric acid at 110—120° to *iso*nicotinic acid. The *platinichloride* forms glistening, reddish-yellow needles and melts and decomposes at about 300°; the *aurichloride* crystallises in light yellow needles and melts at 208—210°.

4-*Cyanoquinoline* prepared from the amide by the action of thionyl chloride or phosphoric oxide, forms colourless crystals, melts at 95°, and sublimes rapidly at 240—245°, forming long needles. The *platinichloride* forms large, reddish-yellow crystals, and, when heated, chars without melting. The *aurichloride* crystallises in small needles and melts at 232°. 4-Cyanoquinoline is not hydrolysed by concentrated hydrochloric acid at 180° or by boiling potassium hydroxide solution, but with alcoholic potassium hydroxide at 160°, cinchonic acid is formed. G. Y.

Abnormal Salts of Pyridone and Lutidone. P. Petrenko-Kritschenko and F. Stamoglu (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 706—710).—*Lutidone phenylhydrazone*, $C_{13}H_{15}N_3$, separates from alcohol in crystalline plates melting at 125°. By heating lutidone (1 mol.) with hydroxylamine hydrochloride (1 mol.) or with ammonium chloride (1 mol.) or with normal lutidone hydrochloride (1 mol.), a comparatively stable *lutidone hydrochloride* of the composition $(C_7H_9ON)_2,HCl$ is obtained, which crystallises in plates melting at 247° and is readily soluble in alcohol or water; the corresponding platinichloride could not be isolated, as it decomposes into the normal platinichloride and lutidone. The corresponding *hydrobromide*, $(C_7H_9ON)_2,HBr$, is readily soluble in water and separates in crystals melting at 250°. The *hydriodide* melts at 235°, and when crystallised together with iodine from alcohol yields a *polyiodide*, $(C_7H_9ON)_2HI_3$, separating in dark brown crystals which melt at 165° and are readily soluble in alcohol.

Pyridone yields similar compounds. The *hydrochloride*,

$$(C_5H_5ON)_2,HCl,H_2O,$$

melts at 110°, the *hydrobromide* ($+H_2O$) at 112°, and the *hydriodide* ($+H_2O$) at 140°; all three salts are readily soluble in water or alcohol.

These salts probably have a diammonium structure, the formula of the hydrochloride of pyridone being

$$CO{<}{\begin{matrix}CH\colon CH\\ CH\colon CH\end{matrix}}{>}NH_2\cdot NHCl{<}{\begin{matrix}CH\colon CH\\ CH\colon CH\end{matrix}}{>}CO\,;$$

one of the ammonium residues plays the part of a base, whilst the other acts as an acid group. T. H. P.

Cinchomeronic Acids and their Esters. ALFRED KIRPAL (*Monatsh.*, 1902, **23**, 929—936. Compare Kaass, Abstr., 1902, i, 564).—3-Methyl 4-hydrogen cinchomeronate crystallises in colourless prisms, melts at 182° (Kaass, m. p. 160°), and when neutralised with ammonia gives a blue precipitate with copper acetate. *Cinchomeron-3-amic acid*, $CO_2H{\cdot}C_5NH_3{\cdot}CO{\cdot}NH_2$, formed by the action of ammonia on β-methyl hydrogen cinchomeronate, crystallises in delicate leaflets, and melts, loses water, and resolidifies at 200°, being converted into cinchomeronimide. 3-Amino*iso*nicotinic acid, formed by the action of bromine and sodium hydroxide on cinchomeronamic acid, melts and decomposes at 292° (compare Blumenfeld, Abstr., 1896, i, 60), and on diazotisation and warming yields *3-hydroxy*iso*nicotinic acid* which crystallises from water in six-sided plates, melts and decomposes at 315°, gives a red coloration with ferric chloride, and on distillation yields 3-hydroxypyridine. G. Y.

5-Nitro-8-methoxyquinoline and Derivatives. GEORGES FREYSS and AD. PAIRA (*Bull. Soc. ind. Mulhouse*, 1902, **72**, 239—244).—*5-Nitro-8-methoxyquinoline*, prepared from *m*-nitro-*o*-anisidine by a modification of Knueppel's method (Abstr., 1891, i, 391), crystallises in slender, yellow needles, melts at 151°, and is almost insoluble in cold water, but readily so in alcohol and boiling toluene. The corresponding amine, obtained by reduction of the foregoing compound, furnishes an acetyl derivative which, unlike the homologous 5-acetylamino-8-ethoxyquinoline, is physiologically inactive. 8-Methoxyquinoline, prepared by Skraup's method from *o*-anisidine or from the amine already mentioned, forms large crystals, melts at 46·5°, and boils at 282° under 742 mm. pressure (compare Bedall and Fischer, Abstr., 1882, 412, and Skraup, Abstr., 1883, 92). T. A. H.

Indogenides with Tinctorial Properties. EMILIO NOELTING (*Bull. Soc. ind. Mulhouse*, 1902, **72**, 236—238. Compare Baeyer, Abstr., 1884, 73).—Protocatechualdehyde, when warmed with indoxylic acid in alcohol solution, furnishes an *indogenide*,

$$C_6H_3(OH)_2{\cdot}CH{:}C{<}{}^{CO}_{NH}{>}C_6H_4,$$

which separates on addition of water in brown flocks; it is soluble in solutions of sodium hydroxide, forming a violet liquid which is decolorised by sodium hyposulphite. Its tinctorial properties are similar to those of indandione derivatives, but the tints produced are less brilliant.

Piperonal indogenide, prepared in a similar manner, separates from acetic acid in orange-coloured crystals, melts at 221°, dissolves in sulphuric acid to a Bordeaux-red colour, and has no tinctorial properties.

The *indogenide* of dimethylaminobenzaldehyde forms reddish-brown needles, melts at 226—227°, and is readily soluble in organic liquids. It forms salts with acids and dyes silk and tannin-mordanted cottons

in dull red shades. p-*Aminobenzaldehyde indogenide* crystallises in reddish-brown needles and dyes silk and mordanted cotton in salmon tints. T. A. H.

Oxidation of *o*-Phenylenediamine. FRITZ ULLMANN and F. MAUTHNER (*Ber.*, 1902, 35, 4302—4306).—The base, $C_{12}H_{10}N_4$, obtained by Griess (*J. pr. Chem.*, 1860, [ii], 3, 142) by oxidising *o*-phenylenediamine with ferric chloride, was found later, by Rudolph (Abstr., 1880, 162), to contain oxygen, the formula $C_{24}H_{18}ON_6$ being assigned to it; Fischer and Hepp (Abstr., 1890, 800) demonstrated that Griess's base was diaminophenazine. It is now found that in this oxidation the diaminophenazine is always accompanied by 3-*amino-2-hydroxyphenazine*, the proportion of the latter increasing with the amount of free hydrochloric acid used in the oxidising mixture. The product of the oxidation, which consisted of a mixture of hydrochlorides in dark brown crystals, was treated with excess of dilute sodium hydroxide, when the diaminophenazine separates as orange-red crystals, whilst the aminohydroxyphenazine goes into solution. Addition of acetic acid to this solution causes the latter compound to separate in orange or dark yellow crystals. By increasing the quantity of free hydrochloric acid present in the oxidation, the aminohydroxyphenazine becomes the main product. The *nitrate* crystallises in needles which dissolve in water to a red solution having a faint green fluorescence. 2-*Acetoxy*-3-*acetylaminophenazine* crystallises in colourless needles melting at about 230°. 2-*Hydroxy*-3-*acetylaminophenazine*, prepared by dissolving the diacetyl derivative in warm sodium hydroxide, crystallises in reddish-brown needles which do not melt at 340°. On heating the aminohydroxyphenazine with 20 per cent. sulphuric acid under pressure at 200° for 6 hours, it is converted into 2 : 3-dihydroxyphenazine (m. p. 226°). When treated with *o*-phenylenediamine and benzoic acid, hydroxyaminophenazine gives homofluorindine. K. J. P. O.

Conversion of Hydrazones into Oximes. HUGO LUDWIG FULDA (*Monatsh.*, 1902, 23, 907—920. Compare Zink, Abstr., 1902, i, 34). —When boiled with excess of hydroxylamine hydrochloride in alcoholic solution, the phenylhydrazones of the following aldehydes and ketones are converted into the corresponding oximes: benzaldehyde, *m*-hydroxybenzaldehyde, protocatechualdehyde, vanillin, furfuraldehyde, acetone, methyl ethyl ketone, methyl *ter.*-butyl ketone, methyl hexyl ketone, methyl nonyl ketone, camphor, fluorenone, acetophenone, phenyl ethyl ketone, *p*-tolyl methyl ketone, phenylacetone, diphenylacetone, α-naphthyl methyl ketone, benzylideneacetone, and pyruvic acid.

Phenylhydrazones of the following do not undergo the reaction: œnanthaldehyde, *o*- and *p*-hydroxybenzaldehydes, anisaldehyde, methylvanillin, piperonal, cuminaldehyde, cinnamaldehyde, benzophenone, and isatin.

Methylvanillinoxime crystallises in long, glistening, colourless prisms and melts at 94—95°.

Methylhexylketoxime forms a slightly yellowish-green oil, which boils at 123—125° under 25 mm. and at 136—138° under 40 mm. pressure. G. Y.

Butylchloralantipyrine. BORTOLO CALDERATO (*Chem. Centr.*, 1902, ii, 1387; from *Boll. Chim. Farm.*, 41, 669—671).—*Butylchloralantipyrine*, prepared by condensing butylchloral hydrate with antipyrine, crystallises from water in yellow crystals, melts at 70—71°, and on sublimation forms a white mass which has the same melting point. When an aqueous solution of equivalent quantities of butylchloral hydrate and antipyrine is left for some time, white crystals of the same composition, but melting at 68—69°, are obtained. Butylchloralantipyrine is readily soluble in alcohol, ether, or chloroform, dissolves in 15·12 parts of water at 25°, and is not attacked by warm potassium hydroxide solution; its alcoholic solution gives a red coloration with ferric salts, and, unlike hypnal, does not reduce Fehling's solution, even on heating. E. W. W.

Phthalyl Green. ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. ind. Mulhouse*, 1902, 72, 268—279. Compare Abstr., 1899, i, 155).—Since this dye is produced, not only by condensing phthalyl tetrachloride with dimethylaniline, but also by the condensation of the latter with tetramethyldiaminophenyloxanthranol (Abstr., 1901, i, 350) in presence of phosphorus oxychloride, the formula

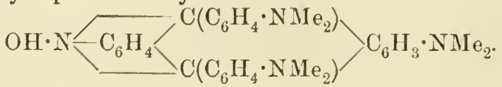
$$C_6H_4{<}{\begin{matrix}CCl(C_6H_4\cdot NMe_2)\text{—}\\ C(OH)(C_6H_4\cdot NMe_2)\end{matrix}}{>}C_6H_3\cdot NMe_2 \text{ or}$$

$$C_6H_4{<}{\begin{matrix}C(:C_6H_4:NClMe_2)\text{—}\\ C(OH)(C_6H_4\cdot NMe_2)\end{matrix}}{>}C_6H_3\cdot NMe_2$$

is proposed for it, derived from the diphenylanthracene dihydride described by Linebarger (Abstr., 1892, 722). These formulæ are also derivable from that of malachite green, to which phthalyl green shows some resemblance, by the joining up of two benzene residues by the divalent radicle $NMe_2\cdot C_6H_4\cdot C\cdot OH$, and are selected in place of the isomeric structures having the chlorine and the hydroxyl in interchanged positions, because all amino-dyes of the triphenylmethane group have at least two amino-groups in the *para*-position to the methane carbon atom.

The *free base* of phthalyl green, obtained by addition of sodium carbonate to an aqueous solution of the dye, crystallises from chloroform on addition of boiling alcohol, in colourless needles, melts at 152°, and becomes coloured on exposure to air. It is represented by the formula $C_6H_4{<}{\begin{matrix}C(OH)(C_6H_4\cdot NMe_2)\\ C(OH)(C_6H_4\cdot NMe_2)\end{matrix}}{>}C_6H_3\cdot NMe_2$.

When phthalyl green is warmed for a few minutes with an alcoholic solution of hydroxylamine hydrochloride and sodium acetate, a *condensation product* is formed which crystallises in colourless needles, melts at 239—240°, and is readily soluble in chloroform, less so in alcohol. A *derivative* similarly obtained from phenylhydrazine hydrochloride and the dye forms pale yellow prisms, melts at 288°, is nearly insoluble in organic liquids with the exception of chloroform, and becomes coloured on exposure to air. The former substance should be probably represented by the formula



T. A. H.

Aromatic Guanidines. FREDERICK J. ALWAY and FREDERICK W. VIELE (*Amer. Chem. J.*, 1902, 28, 292—297).—In preparing triphenylguanidine by the interaction of aniline and diphenylcarbodi-imide, Marckwald (Abstr., 1896, i, 30) found that pentaphenyldiguanide was formed in considerable quantity as a by-product. The formation of a diguanide was not always proved by Marckwald in analogous actions of aromatic amines on diarylcarbodi-imides studied by him.

m-Toluidine resembles *p*-toluidine (compare Marckwald, *loc. cit.*) in its action on diphenylcarbodi-imide, but under certain conditions diphenyl-*m*-tolylguanidine is the only product.

*Tetraphenyl-*m*-tolyldiguanide* melts at 136°; it is readily soluble in acetone and benzene and sparingly so in ether, alcohol, or light petroleum. The *platinichloride* melts and decomposes at 140°.

*Diphenyl-*m*-tolylguanidine*, $C_7H_7 \cdot N \colon C(NHPh)_2$, is best prepared from diphenylthiocarbamide, *m*-toluidine, and lead hydroxide; it melts at 132°, is very soluble in hot alcohol and in hot benzene, but insoluble in water. The *nitrate* melts and decomposes at 179°, the *hydrochloride* melts at 195°, and the *platinichloride* at 237°. A. McK.

Wessel's Dicarbo-base. CARL SCHALL (*J. pr. Chem.*, 1902, [ii], 66, 576—579. Compare Abstr., 1901, i, 766).—The action of methyl iodide on Wessel's base leads to the formation of a ψ-methiodide, $C_{26}H_{20}N_5Me,MeI$, which resembles acridinium ψ-methiodide (Hantzsch and Kalb, Abstr., 1900, i, 113). With silver sulphate, it yields an *oil* which crystallises and is soluble in water. With aqueous sodium hydroxide, the ψ-methiodide yields phenyliminodiphenylurazole (Abstr., 1900, i, 464) and a *substance* which forms microscopic, orange-coloured needles, melts at about 250°, is soluble in acids, but not easily so in other solvents.

Triphenylguanidine and 4-phenylthiosemicarbazide react at 180—190° yielding hydrogen sulphide, ammonia, aniline, and a *compound*, $C_{14}H_{12}N_4S$ (?), which forms microscopic, white crystals melting at 209—210° (corr.). G. Y.

Azoxybenzaldehydes. FREDERICK J. ALWAY (*Amer. Chem. J.*, 1902, 28, 475—480).—The compound obtained by Meister, Lucius, and Brüning from *p*-nitrobenzylaniline (D.R.-P. 111384) is identical with the *p*-azoxybenzaldehyde and its anilide described by the author (Abstr., 1902, i, 697); the patented process gives a yield of 75—80 per cent., and is therefore to be preferred to other methods.

When a solution of *p*-azoxybenzaldehyde in concentrated sulphuric acid is heated at 110—120°, it is converted into a substance which has the characters of an oxyazo-compound.

By the electrolytic reduction of *m*-nitrobenzaldehyde, the *N*-*m*-formylphenyl ether of *m*-nitrobenzaldoxime is first formed; it separates from a solution in boiling pyridine as a grey, granular solid, and by further reduction is converted into an azoxy-compound, probably

$$ON_2(C_6H_4 \cdot CH\overset{O}{\frown}N \cdot C_6H_4 \cdot CHO)_2.$$

m-*Azoxybenzaldehyde* may be obtained by the action of ferric chloride on the products of the electrolytic reduction of *m*-nitrobenzaldehyde,

by treating *m*-nitrobenzaldehyde with zinc dust and ammonium chloride, or by boiling the insoluble compound $(C_7H_5NO)_x$, described by Bamberger and Friedmann (*Ber.*, 1895, **28**, 250), with alcohol and treating the filtrate with aqueous alkali. It crystallises in colourless needles, melts at 129°, and is soluble in benzene, acetic acid, or hot alcohol; its *phenylhydrazone* forms small, orange-coloured needles, and melts at 198°. E. G.

Derivatives of Azobenzene and Hydrazobenzene. By Paul Freundler and L. Béranger (*Bull. Soc. chim.*, 1902, [iii], **27**, 1106—1113. Compare Abstr., 1902, i, 405).—4 : 4'-*Dinitrodiacetylhydrazobenzene*, $N_2Ac_2(C_6H_4{\cdot}NO_2)_2$, obtained by nitrating diacetylhydrazobenzene or its molecular compound with azobenzene (*loc. cit.*), crystallises in pale yellow leaflets, melts at 186—187°, and is slightly soluble in alcohol or ether. When hydrolysed with alcoholic sodium hydroxide, there is formed 4 : 4'-*dinitrohydrazobenzene*, a red, resinous substance, soluble in alkalis with formation of a blue liquid which, on exposure to air, furnishes 4 : 4'-dinitroazobenzene. When treated with ammonium sulphide, the red resin is converted into Werner and Stiasny's supposed 4 : 4'-dinitrohydrazobenzene (Abstr., 1900, i, 194), for which the authors suggest the tautomeric structure $N_2(:C_6H_4:NO{\cdot}OH)_2$; this is reconverted into the true 4 : 4'-dinitrohydrazobenzene by prolonged heating of its solution in alkalis. These substances were obtained in an unsuccessful attempt to apply Friedel and Crafts' reaction to the preparation of azo-ketones and azo-aldehydes. The latter have now been prepared by reducing with zinc dust and alcoholic soda a mixture of nitro-derivatives, one of which contains the requisite oxygenated group, and oxidising the unsymmetrical hydrazo-compound first formed (compare Loeb, Abstr., 1898, i, 654). *p*-Benzeneazobenzaldehyde has thus been obtained; it melts at 120° and furnishes a hydrazone melting at 166° (compare Alway, Abstr., 1902, i, 697).

In the preparation of the diacetyl compound, a molecular compound of diazobenzene with diacetylhydrazobenzene, $2N_2Ac_2Ph_2,N_2Ph_2$, was obtained, which forms orange-red, monoclinic prisms melting at 98·5—99°. T. A. H.

Benzeneazo-*p*-benzaldehyde and its Derivatives. By Paul Freundler and De Laborderie (*Compt. rend.*, 1902, **135**, 1116—1118. Compare Abstr., 1902, i, 650).—It was thought possible to obtain this aldehyde by condensing nitrosobenzene with *p*-aminobenzaldehyde, but attempts to prepare the latter compound were unsuccessful. The oxime of the aldehyde, $NPh:N{\cdot}C_6H_4{\cdot}CH:NOH$, is, however, formed by boiling nitrosobenzene with *p*-aminobenzaldoxime in a mixture of alcohol and acetic acid. It melts at 143° and is very sparingly soluble in cold alcohol, but easily so in acetone. Even at 100°, dilute acids do not saponify it completely, but it is decomposed by nitrous acid; at the same time, however, some secondary products are formed which render the isolation of the aldehyde difficult.

Benzeneazo-*p*-benzaldehyde, when oxidised, gives the corresponding

acid (melting point 238°). When heated at 180° with acetic anhydride and sodium acetate, it gives *benzeneazocinnamic acid*,

$$NPh\colon N\cdot C_6H_4\cdot CH\colon CH\cdot CO_2H,$$

which may also be obtained by heating *p*-aminocinnamic acid with nitrosobenzene in a mixture of alcohol and acetic acid. This acid crystallises from benzene in pink leaflets, which are sparingly soluble in alcohol or acetic acid, and melts and decomposes at 245°. With phosphorus pentachloride, it gives a chloride from which an amide, a methyl ester, and an ethyl ester have been prepared. The *amide* forms reddish-orange plates which melt at 228—229° and are soluble in acetone; the *methyl ester* is formed in red needles which melt at 145° and are sparingly soluble in alcohol or benzene; the *ethyl ester* is obtained in red prisms which melt at 101—102°. Ammoniacal alcohol does not attack the methyl ester, even in sealed tubes at 100°.

From benzeneazo-*p*-benzoic acid, the authors have prepared benzeneazostyrene and benzenehydrazocinnamic acid. J. McC.

o- and p-Nitrobenzenesulphonic Acids. TH. WOHLFAHRT (*J. pr. Chem.*, 1902, [ii], 66, 551—557. Compare Blanksma, Abstr., 1900, i, 482).—*p*-Chloronitrobenzene is converted by alcoholic sodium disulphide into 4 : 4′-*dinitrodiphenyl disulphide*, which crystallises in white needles and melts at 181°, and with sodium hydroxide in alcoholic solution yields a deep bluish-red coloration which disappears on addition of acid or when exposed to the air. The action of sodium disulphide on *p* chloronitrobenzene in 66 per cent. alcohol leads to the formation of a substance which melts at 140—145° and is probably a mixture of di- and poly-sulphides with *p*-nitrophenylmercaptan melting at 78°.

4 : 4′-Dinitrodiphenyl sulphide is oxidised by nitric acid, yielding nitrobenzene-*p*-sulphonic acid.

Electrolytic reduction of potassium *p*-nitrobenzenesulphonate in alkaline solution with a nickel cathode leads to the formation of potassium azobenzene-4 : 4′-disulphonate, $C_{12}H_8O_6N_2S_2K_2,2\frac{1}{4}H_2O$, and potassium hydrazobenzene-4 : 4′-disulphonate, which, by boiling concentrated hydrochloric acid, is converted into azobenzenedisulphonic acid and *p*-sulphanilic acid.

On electrolytic reduction of potassium nitrobenzene-*o*-sulphonate, neither the corresponding azo- nor the hydrazo-derivative can be isolated.

o-Sulphanilic acid is obtained on reduction of ammonium *o*-nitrobenzenesulphonate in alkaline solution or on boiling the alkali salt with zinc dust and water. *o*-Sulphanilic acid does not yield an azo-derivative on treatment with potassium permanganate. G. Y.

Diazoanhydrides. LUDWIG WOLFF [with P. BOCK, GUIDO LORENTZ, and PAUL TRAPPE] (*Annalen*, 1902, 325, 129—195. Compare Abstr., 1900, i, 583).—The *anhydride* of ethyl diazoacetoacetate,

$$\begin{matrix}O\cdot CMe \\ | \\ N{=\!=}N\end{matrix}\!\!>\!C\cdot CO_2Et,$$

is obtained from ethyl acetoacetate in the following manner: ethyl *iso*nitrosoacetoacetate is prepared by adding a concentrated solution of sodium nitrite to a solution of ethyl acetoacetate in acetic acid and extracting the nitroso-compound after the addition of water by means of ether; to the solution obtained by reducing the nitroso-compound by zinc filings and sulphuric acid, a solution of sodium nitrite is then slowly added; from the resulting mixture, the diazoanhydride is extracted by ether; it is an oil which is purified by distilling in steam; it has a sp. gr. 1·1537 at 0°, and boils, although not without decomposition, at 102—104° under 12 mm. pressure; at 110°, it decomposes violently, ethyl *iso*succinate being formed; it is soluble in concentrated hydrochloric acid, the solution slowly decomposing with evolution of gas; dilute sodium hydroxide acts but slowly, but at a higher temperature decomposition is rapid. Attempts to prepare the acid were unsuccessful.

The *anhydride* of diazobenzoylacetone, $O{<}{}^{CMe}_{N:N}{>}CBz$, is prepared from *iso*nitrosobenzoylacetone, which is obtained from benzoylacetone by a method similar to that just described for ethyl *iso*nitrosoaceto-acetate (compare Ceresole, Abstr., 1884, 1167); the *iso*nitroso-compound is reduced with zinc amalgam and sulphuric acid, and the amino-derivative directly diazotised without being isolated; the diazoanhydride separates directly and is purified by recrystallisation from alcohol; it forms plates which have a faint greenish-yellow tinge and melt at 65—66°; it is soluble in concentrated hydrochloric acid, insoluble in alkalis, and decomposed with evolution of nitrogen when boiled with water or acids; it is not acted on by sodium sulphide, potassium acetate, hydrogen sulphide, or iodine; when heated, decomposition is violent, an amorphous substance and an oil smelling of benzyl methyl ketone being formed; it reduces Fehling's solution and colours alcoholic α-naphthol deep blue. When boiled with aqueous sodium hydroxide, acetic and benzoic acids and tarry substances are produced.

The *anhydride* of *diazoacetylacetone,* $O{<}{}^{CMe}_{N:N}{>}C{\cdot}COMe$, is obtained from acetylacetone by means similar to those used for the diazoanhydrides just described; it is a pale yellow oil, somewhat soluble in water, and has not hitherto been obtained quite free from dimethyldiacetylpyrazine.

The diazoanhydrides decompose in a characteristic manner with cold alkalis: $\begin{matrix}O\cdot CR\\ |\\ N{=\!=}N\end{matrix}{>}C{\cdot}COR' + H_2O = R{\cdot}CO_2H + R'{\cdot}CO{\cdot}CH{<}\begin{matrix}N\\ \|\\ N\end{matrix}$. The anhydride of ethyl diazoacetoacetate dissolves in a cold saturated solution of barium hydroxide with a yellow coloration; acetic acid and the products of decomposition of ethyl diazoacetate, namely, chloroacetic acid and glycollic acid, were obtained from the solution, the former being obtained by the action of hydrochloric acid, and the latter by the action of sulphuric acid on the alkaline solution of the diazoanhydride. When treated with very dilute alkali or with concentrated ammonia, the anhydride of diazobenzoylacetone yields diazoacetophenone (m. p. 49—50°. Compare Angeli, Abstr., 1893, i, 570); by

cold sulphuric acid, it is converted into benzoylcarbinol (m. p. 84—85°), and by iodine, into di-iodoacetophenone; the latter, when exposed to light in moist chloroform solution, was found to decompose into phenylglyoxal (m. p. 72—73°).

When boiled with water, these diazoanhydrides undergo a hydrolytic decomposition; the anhydride of ethyl diazoacetoacetate gives the mono-ester of *iso*succinic acid, and diazobenzoylacetone anhydride yields benzyl methyl ketone; in these reactions, a remarkable isomeric change has taken place, a hydroxyl group having exchanged places with a methyl and a phenyl group respectively, thus:

$$O{<}{\substack{CMe\\N:N}}{>}C\cdot CO_2Et + H_2O = N_2 + COMe\cdot CH(OH)\cdot CO_2Et \longrightarrow$$

$$OH\cdot CO\cdot CHMe\cdot CO_2Et;\ \text{and}\ O{<}{\substack{CMe\\N:N}}{>}C\cdot COPh + H_2O = N_2 +$$

$$COMe\cdot CH(OH)\cdot COPh \longrightarrow COMe\cdot CHPh\cdot CO\cdot OH \longrightarrow COMe\cdot CH_2Ph + CO_2.$$

The anhydride of ethyl diazoacetoacetate, when heated at (about) 110°, decomposes, yielding a distillate of ethyl *iso*succinate (b. p. 196—197°); at the same time, small amounts of the mono-ester of *iso*succinic acid and ethyl propionate are formed. The benzyl methyl ketone (b. p. 210—212°), obtained from the anhydride of diazobenzoylacetone, yields a *semicarbazone*, which forms white, prismatic crystals melting at 188—189°, and is identical with that obtained from the synthetical ketone; phenyl ethyl ketone, which might possibly have been formed in this reaction, yields a *semicarbazone* crystallising in needles and melting at 178—179°.

Benzoylacetonediazoanhydride reacts in dilute alcoholic solution with potassium cyanide, producing the *potassium* salt of acetophenoneazocyanide, $OK\cdot CPh\dot{:}CH\cdot N\dot{:}N\cdot CN$; this salt, which can also be obtained under the same conditions from diazoacetophenone, crystallises in lustrous, yellow plates which explode when heated or when treated with sulphuric acid; it is neutral in aqueous solution, gives a brown-red coloration with ferric chloride, a precipitate with lead acetate and silver nitrate, and hydrogen cyanide is formed when it is boiled with sodium hydroxide. The free *acid* is obtained by adding a very dilute solution of the salt to an excess of cold sulphuric acid, and crystallises in colourless leaflets (contrast with the *coloured* benzenediazocyanides), which decompose with evolution of gas at 72°, give, in alcoholic solution, a faint coloration with ferric chloride, and are soluble in alkalis with a yellow colour. The acid is monobasic towards phenolphthalein; it dissolves in concentrated hydrochloric acid, but with decomposition. *Acetophenoneazocarbamide*, $COPh\cdot CH_2\cdot N\dot{:}N\cdot CO\cdot NH_2$, is formed when a solution of the acid just mentioned (or the acid itself) is poured into boiling dilute sulphuric acid, and crystallises in nearly colourless leaflets, which sinter at 210° and melt and evolve gas at 217°; it gives no coloration with ferric chloride, but dissolves in sodium hydroxide; from this solution, an acid can be precipitated, but when the solution is boiled, the carbamide is converted into *hydroxyphenyltriazine*, $CPh{<}{\substack{CH\text{——}N\\N\dot{:}C(OH)}}{>}N$, which is obtained from the yellowish-red, alkaline solution on acidification and crystallises in pale yellow

needles or small plates melting at 234°, and giving no coloration with ferric chloride. In sodium carbonate, it slowly dissolves without change.

The anhydride of ethyl diazoacetoacetate, when heated with ammonium acetate in dilute alcoholic solution, yields *ethyl 5-methyltriazole-4-carboxylate*, $\begin{matrix} N = N \\ | \\ NH\cdot CMe \end{matrix}\!\!>\!C\cdot CO_2Et$, which crystallises in white prisms melting at 161—162° and has feebly acid properties. On hydrolysis with concentrated potassium hydroxide, *5-methyltriazole-4-carboxylic acid* is obtained, crystallising, with H_2O, in flattened needles or plates, and melting and decomposing, when rapidly heated, at 235°; on oxidation, it gives triazole-4 : 5-dicarboxylic acid (m. p. 201°; compare Bladin, Abstr., 1893, 375; 1894, 76). If a dilute solution of this diazoanhydride to which some concentrated ammonia has been added is kept for some weeks, the ammonium salt of *hydroxyacetyltriazole* is formed with the elimination of alcohol, from which the triazole, $NH<\begin{matrix} C(OH) \\ N = N \end{matrix}>C\cdot COMe$, is obtained as colourless needles or small prisms, melting, with evolution of gas, at 128—129°; it gives a deep red coloration with ferric chloride, and behaves as a monobasic acid towards phenolphthalein; the *silver* salt is an insoluble, white powder. Its *semicarbazone* forms small needles melting and evolving gas at 201°, has the acid character of a phenol, and gives a green coloration with ferric chloride in alcoholic, and a blue coloration in aqueous, solution.

With phenylhydrazine, the anhydride of ethyl diazoacetoacetate reacts in acetic acid solution at the ordinary temperature, yielding a mixture of the phenylhydrazone of phenylmethylketopyrazolone (m. p. 155°; Knorr, Abstr., 1887, 602) and *ethyl 1-anilino-5-methyltriazole-4-carboxylate*, $NHPh\cdot N<\begin{matrix} CMe \\ N:N \end{matrix}>C\cdot CO_2Et$, which is separated from the pyrazolone by taking advantage of its insolubility in ether; it crystallises in needles melting at 162°; the *acid* crystallises in needles or leaflets with H_2O, and melts, when anhydrous, at 162°; the *silver* salt is insoluble. On heating the acid with water at 190°, *1-anilino-5-methyltriazole*, $CH<\begin{matrix} CMe \\ N:N \end{matrix}>N\cdot NHPh$, is obtained; it is crystalline and is a very feeble base. When *as*-phenylmethylhydrazine is substituted for phenylhydrazine, *ethyl 1-methylanilino-5-methyltriazole-4-carboxylate*, $NMePh\cdot N<\begin{matrix} N:N \\ CMe \end{matrix}>C\cdot CO_2H$, is obtained as an oil which, on hydrolysis, yields the *acid*; the latter crystallises in needles or plates with H_2O, and melts and evolves gas at 125° when hydrated, and at 148° when anhydrous.

All attempts to obtain a pyrazolone derivative from the anhydride of diazotetronic acid and phenylhydrazine were unsuccessful; the osazone of diketobutyrolactone (m. p. 244°) was alone formed.

Semicarbazide and the anhydride of ethyl diazoacetoacetate give *ethyl 1-carbamido-5-methyltriazole-4-carboxylate*,

$$NH_2\cdot CO\cdot NH\cdot N<\begin{matrix} N:N \\ CMe \end{matrix}>C\cdot CO_2H,$$

which crystallises in slender, white needles melting at 201° and dissolves in cold alkali carbonates. The *acid* crystallises in lustrous prisms which sublime at 205°; the *silver* salt is a gelatinous precipitate. The anhydride of diazoacetylacetone, with semicarbazide, yields the *semicarbazone* of 1-*carbamido*-4-*acetyl*-5-*methyltriazole*,

$$NH_2\cdot CO\cdot NH\cdot N{<}{\genfrac{}{}{0pt}{}{N:N}{CMe}}{\gg}C\cdot CMe:N\cdot NH\cdot CO\cdot NH_2,$$

which forms white needles melting and decomposing at 268° and is soluble in alkalis.

Hydroxylamine converts the diazoanhydrides into aziminoles (hydroxytriazoles). *Ethyl* 5-*methylaziminolecarboxylate*,

$$OH\cdot N{<}{\genfrac{}{}{0pt}{}{N:N}{CMe}}{\gg}C\cdot CO_2Et,$$

is obtained from the diazoanhydride of ethyl acetoacetate and hydroxylamine hydrochloride, which are boiled together in the presence of dilute alcohol and sodium carbonate; the ester crystallises in large prisms melting at 147—148°, gives a red coloration with ferric chloride, and is a strong, monobasic acid. The corresponding *acid* which is purified by conversion into the silver salt, $C_4H_3O_3N_3Ag_2$, crystallises in lustrous prisms with H_2O, decomposes, when anhydrous, at 200—205° and reduces Fehling's solution; on oxidation, it yields the aziminoledicarboxylic acid (m. p. 91—92°) prepared by Zincke (Abstr., 1900, i, 527), which was hitherto the only example of the monocyclic aziminoles. 4-*Benzoyl*-5-*methylaziminole*, $OH\cdot N{<}{\genfrac{}{}{0pt}{}{N:N}{CMe}}{\gg}C\cdot COPh$, prepared from free hydroxylamine and diazobenzoylacetoneanhydride, crystallises in leaflets or slender needles sintering at 180° and decomposing at 190°; it is a monobasic acid and forms an insoluble *silver* salt; with ferric chloride, it gives a violet coloration. When oxidised by alkaline permanganate, this aziminole yields 4-*benzoylaziminole*-5-*carboxylic acid*, $N{<}{\genfrac{}{}{0pt}{}{N\cdot N(OH)}{-C(COPh)}}{\gg}C\cdot CO_2H$, which crystallises in colourless plates melting, with evolution of gas, at 126—127°, gives a yellowish-red coloration with ferric chloride, and precipitates with soluble silver, lead, barium, and calcium salts. Diazoacetylacetoneanhydride and excess of hydroxylamine hydrochloride produce the *oxime* of 4-*acetyl*-5-*methylaziminole*, $OH\cdot N{<}{\genfrac{}{}{0pt}{}{CMe}{N:N}}{\gg}C\cdot CMe:N\cdot OH$, which forms lustrous needles sintering at 208° and decomposing at 213°; it gives a red coloration with ferric chloride, and yields metallic salts, the silver compound being a gelatinous precipitate.

The diazoanhydride of benzoylacetone, when suspended in a dilute cooled alcoholic solution of ammonium hydrosulphide into which hydrogen sulphide was passed for many hours, is converted into a mixture of *benzoylmethylthiodiazole*, $S{<}{\genfrac{}{}{0pt}{}{CMe}{N:N}}{\gg}CBz$, and *acetylphenylthiodiazole*, $S{<}{\genfrac{}{}{0pt}{}{CPh}{N:N}}{\gg}CAc$, which are separated by conversion into mercurichlorides and crystallising these latter from alcohol; from the less soluble *mercurichloride*, $C_{10}H_8ON_2S,HgCl_2$, which crystallises in colourless needles very sensitive to light and melts at 129—130°,

benzoylmethylthiodiazole is obtained by suspending in water and passing in hydrogen sulphide; it crystallises in large leaflets melting at 43°, has a pleasant smell, becomes rapidly red in diffused light, dissolves unchanged in concentrated hydrochloric acid, and is decomposed by hot alcoholic sodium hydroxide, giving a bluish-violet liquid which soon becomes brown; on reduction, hydrogen sulphide is evolved; concentrated nitric acid, in the presence of sulphuric acid, converts it into a crystalline *compound* melting at 112°. With semicarbazide, it yields two *semicarbazones*; the *α-derivative* is the less soluble, and crystallises in needles or prisms melting and decomposing at 217°, from which the original thiodiazole is regenerated by the action of hydrochloric acid; the *β-derivative* crystallises in aggregates of needles melting at 149—150° and is very readily reconverted into the original thiodiazole, but could not be changed into its isomeride. Acetylphenylthiodiazole is prepared from the more soluble mercurichloride, which melts at 60—100°; it crystallises in lustrous, white leaves melting at 70°, and resembles its isomeride very closely, but it does not give a mercurichloride in dilute alcoholic solution; its *semicarbazone* crystallises in needles melting and decomposing at 207°, and is easily reconverted into the thiodiazole by hydrochloric acid. *Acetylmethylthiodiazole*, $S<\substack{CMe \\ N:N}>CAc$, is alone obtained from acetylacetonediazoanhydride and ammonium hydrosulphide; it is purified by conversion into the *mercurichloride* (which crystallises in white needles melting at 127°), and is a pale yellow oil with a powerful odour, which does not solidify at −15°, and is decomposed when distilled; it is dissolved by sodium hydroxide with a red coloration, being at the same time decomposed. Its *semicarbazone* crystallises in flattened needles melting at 230°, and the *oxime* in slender needles melting at 127°. The anhydride of ethyl diazoacetoacetate is also converted into *ethyl methylthiodiazolecarboxylate*, which melts at 35°; the corresponding *acid*, which crystallises with H_2O, melting at 75°. The *methylthiodiazole* obtained from the acid boils at 91° under 38 mm. pressure.

From the diazoanhydride of tetronic acid, no thiodiazole could be obtained; by the action of ammonium hydrosulphide, an orange-coloured substance was formed which rapidly decomposed into tetronic and bitetronic acids.

With β-diketones or the esters of β-ketonic acids, the diazoanhydrides react yielding hydrazones or azo-compounds of little stability, which condense with the elimination of an acyl group, forming a pyrazole. *Ethyl tetronylazoacetoacetate*,

$$\begin{array}{l} CH_2\cdot C(OH) \\ | \\ O\text{———}CO \end{array}>C\cdot N_2\cdot C(CO_2Et):CMe\cdot OH,$$

is prepared by mixing in dilute alcoholic solution the diazoanhydride, ethyl acetoacetate, and potassium acetate, when the potassium salt of the azo-compound is precipitated; the acid crystallises in yellow needles melting at 128°, gives an intense red coloration with ferric chloride, and is decomposed when boiled with water. When the azo-compound is warmed with excess of hydrochloric acid (30 per cent.),

condensation takes place, and the isomeric *glycol ethyl* ester of 4-methylpyrazoledicarboxylic acid,

$$CO_2Et\cdot C\Big<\begin{matrix}CMe—\\N\cdot NH\end{matrix}\Big>C\cdot CO\cdot O\cdot CH_2\cdot CO_2H,$$

separates in colourless needles melting at 181°, and does not give a coloration with ferric chloride; when boiled with sodium hydroxide, glycollic acid and 4-*methylpyrazole*-3 : 5-*dicarboxylic acid*,

$$\begin{matrix}CMe\cdot C(CO_2H)\\ \Vert \\ C(CO_2H)—NH\end{matrix}\Big>N,$$

are formed; the latter crystallises with H_2O in long needles, which become brown at 308° and explode at 312°; it gives insoluble metallic salts, the barium compound crystallising in prisms and the calcium salt in needles. On oxidation with concentrated permanganate, a pyrazoletricarboxylic acid is formed which decomposes at 230° (Buchner, Abstr., 1889, 694, 736).

Ethyl 5-*acetyl*-4-*methylpyrazole*-3-*carboxylate*,

$$CAc\Big<\begin{matrix}CMe—\\NH\cdot N\end{matrix}\Big>C\cdot CO_2Et,$$

prepared from the diazoanhydride of acetylacetone and ethyl acetoacetate, crystallises in woolly needles melting at 121°, and is readily soluble in alkalis; the corresponding *acid* crystallises in prisms or flattened needles with H_2O, melts at 235°, and is oxidised by permanganate to 4-methylpyrazole-3 : 5-dicarboxylic acid (compare Klages, Abstr., 1902, i, 496). Ethyl benzoylacetate condenses with the same diazo anhydride, forming *ethyl* 5-*acetyl*-4-*phenylpyrazole*-3-*carboxylate*,

$$CAc\Big<\begin{matrix}CPh—\\NH\cdot N\end{matrix}\Big>C\cdot CO_2Et,$$

which crystallises in leaflets melting at 113°; the *acid* forms leaflets or flattened needles melting at 208°, and gives precipitates with silver nitrate and lead acetate. With acetylacetone, the diazoanhydride yields 3 : 5-*diacetyl*-4-*methylpyrazole*, $CAc\Big<\begin{matrix}CMe—\\NH\cdot N\end{matrix}\Big>CAc$, which crystallises in needles with H_2O, melting at 76—90° or when anhydrous at 114°, and is readily soluble in alkali carbonates; the *dioxime* crystallises with $\frac{1}{2}H_2O$ in needles melting at 217°, and is soluble in alkali hydroxides, but not in alkali carbonates. With benzoylacetone, 3 : 5-*diacetyl*-4-*phenylpyrazole* is formed, crystallising in needles melting at 134°. From its manner of formation, this substance might be 3 : 5-acetylbenzoyl-4-methylpyrazole, but its oxidation to 4-phenylpyrazoledicarboxylic acid (m. p. 243°; Buchner, Abstr., 1902, i, 236) excludes this possibility.

The diazoanhydride of benzoylacetone condenses with ethyl acetoacetate producing *ethyl* 5-*benzoyl*-4-*methylpyrazole*-3-*carboxylate*,

$$CBz\Big<\begin{matrix}CMe—\\NH\cdot N\end{matrix}\Big>C\cdot CO_2Et,$$

which crystallises in aggregates of needles melting at 119—120°; its *sodium* salt crystallises in lustrous plates; the free *acid* forms aggregates of needles melting at 233°; on oxidation, it is converted into

5-*benzoylpyrazole*-3 : 4-*dicarboxylic acid*, $NH<\begin{matrix}CBz:C\cdot CO_2H\\ N=C\cdot CO_2H\end{matrix}$, which forms prismatic crystals melting with evolution of gas at 220°, and gives crystalline barium and calcium salts. 5-*Benzoyl*-3-*acetyl*-4-*methylpyrazole*, $CBz<\begin{matrix}CMe-\\ NH\cdot N\end{matrix}>CAc$, is prepared from the diazoanhydride just mentioned and acetylacetone, and crystallises in colourless needles melting at 97°; on oxidation, it gives 5-benzoylpyrazole-3 : 4-dicarboxylic acid (m. p. 220°). In the pyrazole derivatives here described, it is uncertain which group occupies the 3 and which the 5 position.

*iso*Nitrosoacetylacetone reacts with phenylhydrazine hydrochloride in aqueous solution, giving 4-*nitroso*-1-*phenyl*-3 : 5-*dimethylpyrazole*, $CMe<\begin{matrix}C(NO)-\\ NPh\cdot N\end{matrix}>CMe$, which crystallises in malachite-green leaflets melting at 94°, and is soluble in hydrochloric acid, forming an olive-green solution, which soon becomes red. By nitric acid, it is converted into 4-*nitro*-1-*phenyl*-3 : 5-*dimethylpyrazole*, which crystallises in colourless needles melting at 103°.

4-*Nitroso*-3 : 5-*dimethylpyrazole*, $CMe<\begin{matrix}C(NO)\\ NH\cdot N\end{matrix}>CMe$, prepared from hydrazine sulphate and *iso*nitrosoacetylacetone, crystallises in blue needles melting at 128° and forms a red sodium salt; by nitric acid, it is converted into 4-nitro-3 : 5-dimethylpyrazole (m. p. 124—126°), which does not give a ferric chloride reaction. 4-*Nitroso*-5 : 3-*phenylmethylpyrazole* is obtained in an analogous manner from *iso*nitrosobenzoylacetone, and crystallises in dark green prisms or plates melting at 153°.

Acetylmethylglyoxime, $OH\cdot N:CMe\cdot CAc:NOH$, is formed by the action of hydroxylamine hydrochloride on *iso*nitrosoacetylacetone, and crystallises in plates melting and decomposing at 128°; its solutions in neutral solvents and in acids soon become green.

Diacetyldimethylpyrazine, $\begin{matrix}CMe\cdot N\cdot CAc\\ CAc\cdot N\cdot CMe\end{matrix}$, is formed in the preparation of the diazoanhydride of acetylacetone, and is produced from the aminoacetylacetone; it is best prepared by reducing *iso*nitrosoacetylacetone with zinc dust and dilute acetic acid and then oxidising the product with sodium nitrite; it crystallises in sulphur-yellow needles melting at 98—99° and is a very weak base; its *semicarbazone* is colourless and melts at 300°. K. J. P. O.

Diazo-compounds. I. Relation between Nitroso- and Diazo-compounds and Diazoethers. ARTHUR HANTZSCH and E. WECHSLER (*Annalen*, 1902, **325**, 226—250).—The nitrosoacylanilides, which are formed either by the action of nitrous acid on acylanilides or of acyl chloride on normal (*syn*-)diazoxides or *iso*-(*anti*-)diazoxides, are undoubtedly represented by the expression $Ar\cdot NAc\cdot NO$; on reduction, they yield the acylanilide and never hydrazines, with hydrochloric acid they give the anilide and nitrosylchloride. When hydrolysed by alkalis, alkali acetate and the normal

(*syn*-)diazoxide are formed, but in alcoholic solution with alkali ethoxide (not in excess) the alkali *iso*diazoxide is produced. Other nitrosoamines, such as *p*-hydroxybenzylphenylnitrosoamine or *p*-anisol-*p*-hydroxybenzylnitrosoamine, only yield *iso*diazoxides, but here hydrolysis takes place only slowly, and at higher temperatures.

The fact that nitrosoacylanilides in alcoholic solution give, on hydrolysis, *iso*diazoxides and not normal diazoxides would lead to the conclusion that the normal diazoxides in this solvent have suffered "alcoholysis" with the formation of a normal (*syn*-)diazo-ether, Ar·N⁚N·OEt. This alcoholysis would be the immediate cause of the hastening of the change of normal into the *iso*diazoxides in alcoholic solution, when there is no excess of alkali, if the normal (*syn*-)diazo-ethers change into the *iso*diazo-ethers more rapidly than the normal into the *iso*diazoxides. But despite the fact that the diazo-ethers are obtained from the silver salts of the *iso*diazoxides, and not from those of the normal diazoxides, they have hitherto been supposed to belong to the normal series as, according to Bamberger (Abstr., 1895, i, 215), they yield on hydrolysis normal diazoxides. The authors find, however, in the case of *p*-bromobenzenediazoethyl ether, whether hydrolysed by aqueous alkali or by potassium ethoxide in ethereal solution, that only the *iso*-(*anti*-)diazoxide is formed. Further, the normal (*syn*-)diazo-ether should be formed by the action of potassium ethoxide on the diazonium chloride; at −18°, only the decomposition products of the normal ether, phenyl ethyl ether, and nitrogen are obtained, whilst at a higher temperature the *iso*diazo-ether is the main product.

Wohl's (Abstr., 1893, i, 200) and Pechmann's (Abstr., 1894, i, 282) observations are confirmed that nitrosobenzanilide yields only benzanilide and ammonia on reduction. More extensive experiments have demonstrated that both nitrosobenzanilide and nitrosoacetanilide give on hydrolysis only the *iso*diazoxides (Bamberger, Abstr., 1897, i, 241). p-*Bromonitrosoacetanilide*, $C_6H_4Br·NAc·NO$, is prepared by passing nitrous oxides into a suspension of *p*-bromoacetanilide in acetic acid until the solid has completely dissolved, forming a green solution, and then precipitating with water; it crystallises in yellow needles which explode at 88° and behaves in every way as do the other nitrosoacylanilides; with potassium cyanide in alcoholic solution, it gives *p*-bromobenzenediazoiminocyanide, $C_6H_4Br·N_2·C(CN)⁚NH$ (m. p. 109—110°). s-*Tribromonitrosoacetanilide*, $C_6H_2Br_3·NAc·NO$, is obtained in a similar manner as a yellow precipitate melting at 93° and decomposing very readily into *s*-tribromoacetanilide and nitrous acid when treated with acids. *Nitrosodiphenylcarbamide*,

NO·NPh·CO·NHPh,

forms a yellow powder melting and decomposing at 82°.

o-*Hydroxybenzylidene*-p-*anisidine*, $OH·C_6H_4·CH⁚N·C_6H_4·OMe$, prepared from salicylaldehyde and *p*-anisidine, forms pale yellow scales melting at 86°. On reduction with sodium amalgam in alcoholic solution, o-*hydroxybenzyl*-p-*anisidine*, $OH·C_6H_4·CH_2·NH·C_6H_4·OMe$, is obtained; it forms a white, crystalline powder melting at 127°. The *nitrosoamine*, $OH·C_6H_4·CH_2·N(NO)·C_6H_4·OMe$, is prepared by treating a solution of the base in hydrochloric acid with sodium nitrite, and

forms red crystals melting at 91°; under no conditions could a normal (*syn*-)diazoxide be obtained from it; with an alkaline solution of β naphthol, it gives *p*-anisolazo-β-naphthol (m. p. 141°). K. J. P. O.

Constitution of Diazotates and Diazohydrates [Diazoxides and Diazohydroxides]. By ARTHUR HANTZSCH (*Annalen*, 1902, **325**, 250—259).—Bamberger has recently expressed the opinion (Abstr., 1900, i, 705) that the diazonium salts are represented by the formula $Ph\cdot N(A){\vdots}N$, and the stable series of diazoxides (the *iso*- or *anti*-diazoxides) by the formula $Ph\cdot N{:}N\cdot OM$, but that the labile series of diazoxides (the normal or *syn*-diazoxides) are constitutionally different from the *iso*diazoxides, and are probably represented by some such expression as $O{<}\begin{matrix} N\cdot Ph \\ | \\ N{-}M \end{matrix}$, whereas the author believes that these latter are stereoisomeric with the *iso*diazoxides. He maintains that all the reactions of the normal diazoxides are only represented by the formula $Ph\cdot N{:}N\cdot OM$, inasmuch as they do not yield alkyl or acyl derivatives of the type $O{<}\begin{matrix} NPh \\ | \\ NAlk(Ac) \end{matrix}$, but they react with phenols with extreme ease, forming azo-derivatives, and so readily suffer the characteristic decomposition into nitrogen and phenols. Moreover, isomerism of two such salts as the potassium normal and *iso*-diazoxides, which depends only on a different place of attachment of the alkali metal, is unique. Further, only when the normal diazoxides are considered as stereoisomerides of the *iso*diazoxides is the analogy seen between these salts and the two series of diazocyanides and diazosulphonates. Attention is also drawn to the fact that ammonium cyanides and hydroxides other than diazonium compounds change isomerically into neutral compounds with the cyano- or hydroxyl groups attached to carbon

$$\begin{matrix} C\diagdown^{V} \\ C{:}N\cdot CN \text{ (or OH)} \\ C\diagup \end{matrix} \longrightarrow \begin{matrix} C\diagdown^{III} \\ \text{(OH or) } CN\cdot C\cdot N \\ C\diagup \end{matrix};$$

the hydroxyl or cyano-group has wandered as a whole in the same manner as, in the author's opinion, occurs in the conversion of the diazonium hydroxides into the normal diazoxides. K. J. P. O.

Benzidines. By KARL ELBS and TH. WOHLFAHRT (*J. pr. Chem.*, 1902, [ii], **66**, 558—575. Compare this vol., i, 203).—The authors have reduced nitrobenzene-*m*-sulphonic acid electrolytically to hydrazobenzene-disulphonic acid and converted the latter substance into benzidine-2 : 2′-disulphonic acid. *o*-Tolidine-2 : 2′-disulphonic acid and 2 : 2′-diaminobenzidine are prepared by similar reactions from *o*-nitrotoluene-*p*-sulphonic acid and *m*-nitroaniline respectively.

Tetra-acetyldiaminobenzidine, $C_{20}H_{24}O_4N_4,3H_2O$, crystallises in colourless needles, loses $3H_2O$ at 105—110°, and melts at 284°. The anhydrous substance is a white, hygroscopic powder easily soluble in alcohol. When diazotised with a limited quantity of sodium nitrite in hydrochloric acid solution, diaminobenzidine forms a reddish-brown liquid which dyes cotton chocolate-brown in an alkaline bath;

with excess of sodium nitrite, a brownish-black powder is formed, insoluble in the usual solvents or in acids or alkalis. With the bisdiazo-derivative of *o*-tolidine-2 : 2′-disulphonic acid in aqueous solution, diaminobenzidine hydrochloride forms deep red, glistening crystals which probably have the constitution $\begin{matrix} N\cdot C_{12}H_4Me_2(SO_3H)_2\cdot N \\ || \qquad\qquad\qquad || \\ N—[C_6H_2(NH_2)_2]_2—N \end{matrix}$.

The bisdiazo-derivative of *o*-tolidine-2 : 2′-disulphonic acid couples with *β*-naphthol, resorcinol, salicylic acid and naphthionic acid with formation of the following derivatives: *β-naphtholbisazoditolyl-2 : 2′-disulphonic acid* is reddish-blue, only slightly soluble in water, and yields a sodium salt which forms a thick, red precipitate and a barium salt, $C_{24}H_{16}O_7N_4S_2Ba$, which is a red powder insoluble in water; *barium resorcinol-bisazoditolylsulphonate*, $C_{20}H_{14}O_8N_4S_2Ba$, is a dark brown powder which is only slightly soluble in water; *sodium 2 : 2′-disulphodi-*o*-tolylbisazosalicylate* forms a brownish-red, aqueous solution; the *barium* salt, $C_{28}H_{18}O_{12}N_4S_2Ba$, is a yellowish-brown powder; *sodium 2′ : 2″-disulphodi-*o*-tolylbisazo-α-naphthylamine-4-sulphonate* forms a red, crystalline precipitate; the aqueous solution is yellowish-red and gives a deep blue precipitate on addition of hydrochloric acid; the *barium* salt, $C_{34}H_{24}O_{12}N_6S_4Ba_2$, forms a red powder. These bisazo-derivatives of *o*-tolidine-2 : 2′-disulphonic acid dye unmordanted cotton only partially (compare Täuber, Abstr., 1890, 782).

*Sodium diacetyl-*o*-tolidine-2 : 2′-disulphonate*,

$$(C_6H_2Me\cdot NHAc\cdot SO_3Na)_2,$$

formed by dissolving sodium tolidinedisulphonate in boiling acetic anhydride, crystallises in white needles containing $3C_2H_6O$, which is lost at 110—115°. If the sodium salt is boiled with acetic anhydride, *sodium tetracetyl-*o*-tolidine-2 : 2′-disulphonate*, $(C_6H_2Me\cdot NAc_2\cdot SO_3Na)_2$, is formed, which crystallises in colourless needles containing $2\frac{1}{2}C_2H_6O$, which is lost at 110—115°. On diazotation and treatment with cuprous chloride, *o*-tolidinedisulphonic acid yields 4 : 4′-*dichloro-5 : 5′-dimethyldiphenyl-2 : 2′-disulphonic acid*, which forms a hard, glistening, vitreous mass which is soluble in water or alcohol. The *barium* salt, $C_{14}H_{10}O_6Cl_2S_2Ba,3\frac{1}{2}H_2O$, crystallises in delicate, white needles.

The following derivatives of benzidine-2 : 2′-disulphonic acid are described:

Bisdiazodiphenyldisulphonic acid, which crystallises in large, colourless needles. *β-Naphtholbisazodiphenyl-2 : 2′-disulphonic acid* is soluble in alkalis or acids, the alkaline solution is yellowish-red, the acid solution bluish-red; the *barium* salt, $C_{22}H_{12}O_7N_4S_2Ba$, is insoluble. 2′ : 2″-*Disulphodiphenylbisazo-α-naphthylamine-4-sulphonic acid* resembles the corresponding *o*-tolidine derivative. 2′ : 2″-*Disulphodiphenylbisazo-α-naphthol-4-sulphonic acid* forms a soluble *sodium* salt, which dissolves in water to a red solution, and a *barium* salt, $C_{32}H_{16}O_{14}N_4S_4Ba$, which is a dark red powder. 2′ : 2″-*Disulphodiphenylbisazo-β-naphthol-3 : 6-disulphonic acid* forms a red *sodium* salt; the *barium* salt, $C_{32}H_{14}O_{20}N_4S_6Ba_3$, is a red, crystalline powder. *Sodium diacetylbenzidine-2 : 2′-disulphonate* crystallises in white needles containing $1\frac{1}{2}C_2H_6O$.

G. Y.

Constitution of the Albumin Molecule. Franz Hofmeister (*Chem. Centr.*, 1902, ii, 1263—1264; from *Naturw. Rundsch.*, 17, 529—545).—The paper contains a list of the various compounds which have been obtained by the decomposition of albumin and some theories as to the constitution of the molecule. According to these, the molecule may be regarded as made up of 125 groups or residues. The amino-acids, which form $\frac{2}{3}$—$\frac{3}{4}$ of the molecule, are probably connected by means of the imino-groups. E. W. W.

Identification of Albumins. Johannes Boes (*Chem. Centr.*, 1902, ii, 1133—1134; from *Ber. Deut. pharm. Ges.*, 12, 220—221). —Experiments have shown that when Riegel's method is used for isolating the albumins from *Liquor ferri albuminati* (*Pharm. Zeit.*, 42, 430), casein and blood-albumin alone form clear solutions, whilst egg-albumin is almost completely precipitated by the concentrated hydrochloric acid. Hence, on diluting the filtrate, the only acid compounds precipitated are those of casein and blood-albumin. The latter is more readily soluble in lime-water than either the acid compound of egg-albumin or that of casein, but the difference in solubility scarcely forms a trustworthy method of identification; an examination of the products of decomposition, therefore, probably still remains the best method. E. W. W.

Preparation of Colourless Albumins from Dark Coloured Plant Juices. A. Rümpler (*Ber.*, 1902, 35, 4162—4164).—The albumins of beet-root juice and other vegetable juices can be obtained colourless by treating the juice, or the crushed plant, with ammonium sulphate and pressing out the liquid, the operations being repeated until a colourless filtrate is obtained. The mass is then extracted with water, the albumins reprecipitated by solid ammonium sulphate, and the precipitate filtered off and washed with ammonium sulphate solution.

The albumins from beet juice, after treatment in this way, yield a colourless solution, from which one of them is precipitated by acetic acid in the cold, whilst the other may be precipitated by alcohol from the filtrate. A. H.

Serum Globulins. Otto Porges and Karl Spiro (*Beitr. chem. Physiol. Path.*, 1902, 3, 277—285. Compare Fuld and Spiro, Abstr., 1901, ii, 67).—Further experiments are given to show that serum globulin is not a single substance. The method of separation used is fractional precipitation with various salts. In the case of some salts, the precipitation overlaps, but, speaking generally, the euglobulin is most easily salted out. The pseudo-globulins are in the later fractions and contain less carbon and nitrogen per cent. W. D. H.

Caseinogen of Asses' Milk. Karl Storch (*Monatsh.*, 1902, 23, 712—730).—The composition of cows' and asses' milk is compared particularly with reference to the caseinogens. The latter contains less solid matter, less fat and proteids, but more sugar than cows' milk, and is more alkaline. By precipitation with neutral salts, two

distinct proteids may be separated from asses' milk, but it is probable that these are united in the original milk. The two proteids are very similar to two extracted previously from cows' milk. E. F. A.

Some of the Salts formed by Casein and Paracasein with Acids; their Relations to American Cheddar Cheese. LUCIUS L. VAN SLYKE and L. B. HART (*New York, Geneva, Agric. Exper. Stat. Bul.*, 1902, No. 214, 53—79; *Amer. Chem. J.*, 1902, 28, 411—438).—Normal cheese contains varying amounts of a substance, soluble in salt solution, having the properties of paracasein lactate. The amount is greatest in new cheese. Large quantities of the substance were produced when cheese was made in presence of lactic acid, whilst without acid only small quantities were formed.

Paracasein forms both unsaturated and saturated salts with acids, the former being soluble in dilute sodium chloride solutions and in hot 50 per cent. alcohol, but insoluble in water. The saturated salts are practically insoluble. The existence of two kinds of salts may account for the results obtained by Danilewsky (*Zeit. physiol. Chem.*, 1883, 7, 227), who supposed that casein consists of two proteids.

The ripening process in normal Cheddar cheese, resulting in the production of soluble nitrogen compounds, begins with unsaturated paracasein lactate and not with paracasein. N. H. J. M.

A Proteid Substance extracted from Maize Grains. E. DONARD and H. LABBÉ (*Compt. rend.*, 1902, 135, 744—746).—The oil was extracted from dried maize grains by means of benzene and the proteid dissolved out with boiling amyl alcohol. The amyl alcohol solution, when treated with benzene, gives a flocculent precipitate of a proteid which is not identical with that obtained from any other cereal. It is termed *maisin*, and its composition is represented by the formula $C_{184}H_{300}O_{51}N_{46}S$. It is insoluble in cold water, but by prolonged boiling it is hydrolysed. It is soluble in methyl alcohol, ethyl alcohol, or acetone, and from these solutions can be precipitated by ether or benzene. From its solution in amyl acetate, it is deposited as a white powder. When heated with aqueous acid solutions, it develops a peculiar odour. It is easily soluble in alkali solutions. Maize contains 4 to 4·5 per cent. of maisin. J. McC.

Proteid Base from the Sperm of the Tunny Fish. C. ULPIANI (*Gazzetta*, 1902, 32, ii, 215—234).—The author first discusses the present state of knowledge concerning the hydrolytic products of the proteid molecule and then describes the preparation and compounds of a proteid base isolated as sulphate from the sperm of the tunny fish (*Tynnus vulgaris*).

The *sulphate*, $C_{56}H_{116}O_9N_{29}(SO_4)_3,4H_2O$, forms a white powder readily soluble in water, from which it is precipitated by concentrated ammonia or ammonium sulphate, or sodium chloride solution, or alcohol. It gives an intense biuret reaction and a distinct reaction with Millon's reagent, and in neutral solution it is precipitated by the alkali salts of phosphotungstic, hydroferrocyanic, picric, and chromic acids; with a solution of Witte's peptone, it also gives an appreciable

precipitate. The *carbonate* ($13H_2O$) has $[\alpha]_D$ $-24\cdot87°$ at 21°; the *molybdate* has the composition $(C_{56}H_{116}O_9N_{29})_3(Mo_7O_{24})_4,15H_2O$; the *tungstate* gives the formula $C_{56}H_{104}O_3N_{29}(W_2O_7)$, the expulsion of water being probably due to condensation in the interior of the molecule.

Hydrolysis of the sulphate by means of dilute sulphuric acid gives rise to various products, only one of which, arginine, has been identified.

The author regards the base as a histone which exists in the tunny sperm in combination with a nucleic acid. T. H. P.

Hydrolysis of Horn. Emil Fischer and Theodor Dörpinghaus (*Zeit. physiol. Chem.*, 1902, 36, 462—486).—In addition to the decomposition products of horn already known, leucine, tyrosine, aspartic acid, glutamic acid, arginine, lysine, and cystin, six other acids have now been isolated by the ester method, namely, glycine, alanine, α-amino*iso*valeric acid, 2-pyrrolidinecarboxylic acid, serine, and phenylalanine.

Cattle horn was hydrolysed and esterified in the usual way, but owing to presence of compounds containing sulphur could not be directly fractionally distilled. The mixture of esters was extracted with petroleum, when, with the exception of serine ester and the compounds containing sulphur, the esters partly pass into solution. Both the dissolved and the undissolved substances are then fractionated. The first fraction of the soluble esters up to 40° contains glycineanhydride; the second fraction, 40—55°, yields *d*-alanine; the third fraction, 55—80°, gives 2-pyrrolidinecarboxylic acid, leucine, and *d*-α-amino*iso*valeric acid. The fourth fraction, 80—85°, contains mainly leucine and 2-pyrrolidinecarboxylic acid. The fraction 85—110° gave only a small quantity of leucine-ester, but a similar fraction obtained by distilling the esters insoluble in petroleum yielded the esters of leucine, aspartic acid, and serine, and a new compound which was very difficult to separate from the serine. The fraction 115—140° of the soluble esters consisted mainly of phenylalanine. A fraction 110—135° of the insoluble esters gave largely *r*-aspartic acid, together with serine, phenylalanine, and glutamic acid. The fraction 140—155° of the soluble esters yielded phenylalanine and glutamic acid together with a little aspartic acid; the corresponding fraction of the insoluble esters consisted chiefly of *r*-glutamic acid. The final fraction of both lots of esters contained pyrrolidonecarboxylic acid, which, up to the present, has not been recognised as a product of proteid hydrolysis; it is probably a secondary product arising from the glutamic acid.

By this process, 40·02 per cent of monoamino-acids were obtained from horn, namely, glycine, 0·34; alanine, 1·2; α-amino*iso*valeric acid, 5·7; leucine, 18·30; 2-pyrrolidinecarboxylic acid, 3·6; serine, 0·68; phenylalanine, 3·0; aspartic acid, 2·5; glutamic acid, 3·0; and pyrrolidonecarboxylic acid, 1·7 per cent. K. J. P. O.

Action of Chloroform on Hæmoglobin. Friedrich Krüger (*Beitr. chem. Physiol. Path.*, 1902, 3, 67—88).—The experiments show that chloroform is not an indifferent reagent towards hæmoglobin, but

changes it into a more insoluble modification without apparently producing any profound chemical alteration. The spectroscopic appearances are described, but this aspect of the question is stated to demand further investigation. W. D. H.

Mesoporphyrin. J. ZALESKI (*Zeit. physiol. Chem.*, 1902, 37, 54—74. Compare Abstr., 1901, i, 434; Marchlewski, Trans., 1900, 77, 1091; Abstr., 1902, i, 636).—Full details for the preparation and purification of mesoporphyrin hydrochloride are given. In many respects, namely, crystallographic, spectroscopic, and general chemical properties, it closely resembles hæmatoporphyrin hydrochloride. It differs, however, in composition (mesoporphyrin hydrochloride probably has the formula $C_{34}H_{38}O_4N_4$,2HCl, hæmatoporphyrin hydrochloride $C_{34}H_{38}O_6N_4$,2HCl) and also in formation of ethers (compare Abstr., 1900, i, 710). When mesoporphyrin hydrochloride is boiled with 5—12 per cent. solutions of hydrogen chloride in methyl or ethyl alcohol for 4—9 hours, *methyl* and *ethyl* ethers are formed and may readily be obtained in a crystalline form. The methyl ether sinters at 190° and melts at 213—214° (uncorr.). The ethyl ether, $C_{34}H_{36}O_4N_4Et_2$, crystallises in flat plates, is strongly doubly refractive, and melts at 202—205°. Both ethers are insoluble in alkalis, but dissolve readily in most organic solvents. They also dissolve sparingly in boiling 9 per cent. hydrochloric acid, and on cooling, crystals of mesoporphyrin are deposited.

Hæmatoporphyrin, when reduced with hydriodic acid or phosphonium iodide, yields mesoporphyrin.

From cryoscopic determinations of the molecular weights in phenol, mesoporphyrin and its derivatives, and also hæmatoporphyrin, must be represented by formulæ containing C_{34}, not C_{17}.

Free mesoporphyrin has acidic properties and forms definite salts which are only sparingly soluble in most solvents. The following have been prepared: *ammonium*, crystallising in small needles; *zinc*, $C_{34}H_{36}O_4N_4Zn$; *copper*, $C_{34}H_{36}O_4N_4Cu$. The ethers are also capable of forming metallic salts, the *copper* salt of the ethyl ether, $C_{38}H_{44}O_4N_4Cu$, forms minute needles, is moderately soluble in chloroform, benzene, or toluene, and melts at 211°. J. J. S.

Crystalline Colouring Matter from Urine. S. COTTON (*J. Pharm. Chim.*, 1902, [vi], 16, 258—261. Compare Abstr., 1900, ii, 293).—The violet-red, crystalline substance obtained by concentration of urine mixed with nitric acid, as formerly described, resinifies on keeping, but is stable in the presence of glacial acetic acid, like hæmin, which it resembles in crystalline form. The absorption spectrum is similar to that of hæmatein.

As the same substance is formed by the action of hydrochloric or sulphuric acid on urine, the author no longer regards it as an oxidation product. G. D. L.

Characterisation of the Sarcommelanin of Man. LEO VON ZUMBUSCH (*Zeit. physiol. Chem.*, 1902, 36, 511—524).—With the object of demonstrating the relation of sarcommelanin to hæmoglobin,

the state of combination of the sulphur in both substances has been investigated. On hydrolysing a large quantity of oxyhæmoglobin with fuming hydrochloric acid, no cystin was obtained, all the sulphur appearing in a more oxidised form. Liver-melanin, when similarly treated, also yielded no cystin. The absence of cystin in the products of hydrolysis of both these pigments shows that they are nearly related; possibly hæmoglobin is converted into melanin by a fermentative process. K. J. P. O.

Amount of Iron in the Sarcommelanin of Man. E. Zdarek and Richard von Zeynek (*Zeit. physiol. Chem.*, 1902, **36**, 493—497).—Mörner's observation that iron is present in human melanotic sarcoma is confirmed, and it is further shown that it is in stable organic combination. It is suggested that sarcommelanins consist of the coloured component of hæmoglobin, hæmatin, but do not contain the proteid group, as has been previously supposed.

K. J. P. O.

Hydrolysis of Triacetyldextrose by Enzymes. S. F. Acree and J. E. Hinkins (*Amer. Chem. J.*, 1902, **28**, 370—386).—An account is given of an investigation of the action of pancreatin, amylopsin, emulsin, maltase, diastase, and takadiastase on triacetyldextrose at 0°. In every case, the enzyme hydrolyses triacetyldextrose with formation of dextrose and acetic acid, but whilst some enzymes, emulsin for example, hydrolyse only a small amount of the compound, others effect a considerable change. Pancreatin seems to be the most active; its activity at 37° is found to be twice as great as at 0°. Pancreatin is also capable of effecting the combination of acetic acid with dextrose, with formation of the dextrose ester. The amount of hydrolysis of triacetyldextrose is dependent on, and nearly proportional to, the quantity of enzyme present; in no case is the hydrolysis complete. E. G.

Action of Emulsin and other Ferments on Acids and Salts. Max Slimmer (*Ber.*, 1902, **35**, 4160—4162).—Several cases have been observed which do not agree with the statement made by Kastle (Abstr., 1902, i, 655) that ionisable substances are not decomposed by ferments. Amygdalinic acid and its sodium salt are readily hydrolysed by emulsin. The sodium salt is also hydrolysed into dextrose and glucomandelic acid by an extract of dried yeast. Sodium glucovanillate is readily hydrolysed by emulsin. Glucosalicylic acid, which will shortly be described, is also slowly hydrolysed by emulsin.

A. H.

Fermentative Fat-hydrolysis. W. Connstein, E. Hoyer, and H. Wartenburg (*Ber.*, 1902, **35**, 3988—4006).—Green (*Proc. Roy. Soc.*, 1890, **48**, 370) and Sigmund (Abstr., 1890, 1455; 1892, 1261) have described the fat-decomposing ferment of seeds; Green states that this action is hindered by the presence of minute quantities of free acid, and finally completely stopped. The authors have made an exhaustive series of experiments, using mainly castor oil seeds as the

source of the ferment, and various fats. Preliminary experiments showed that after a given fat had been subjected to the action of the ferment for a few days, during which the fat was slowly hydrolysed, there was a sudden very rapid hydrolysis of the larger part of the fat. It was found on modifying the conditions that this was to be attributed to the presence of free acid; if acetic or sulphuric acid was added initially, there was no such discontinuity, but the fat was hydrolysed nearly completely in 24 hours. Green was therefore in error in stating that free acid stopped the action of the ferment. Systematic experiments have demonstrated the following facts. 1. The seeds of *Euphorbiaceæ*, and more especially of the castor oil plant, possess this fat-hydrolysing property in the most marked degree. 2. The glycerides of fatty acids are more easily hydrolysed the higher the molecular weight of the acid. 3. The esters (ethyl, methyl, amyl, &c.) of acetic, benzoic, and other acids, are not affected; but methyl oleate is hydrolysed with great rapidity. 4. For good results, the quantity of water present must be at least three times that theoretically necessary. The nature of the acid used seems to be without effect; the optimum concentration appears to lie between $N/10$ and $N/3$. It is essential that the fat should be thoroughly emulsified. 5. Rise of temperature increases the activity of the ferment, but a temperature above 40° is disadvantageous. 6. Alcohol, alkalis, soap, formaldehyde, sodium fluoride, and mercuric chloride all act as poisons to the ferment, but the majority of normal salts are without effect.

Attention is drawn to the fact that this forms the cheapest method of hydrolysing fats. K. J. P. O.

Action of Invertase. VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, **54**, 1215—1216. Compare Abstr., 1902, ii, 127).—The inversion of cane-sugar by invertase is more rapid than with acids, and does not follow the same logarithmic law. Equations to represent both reactions are given and discussed. W. D. H.

Lipase from Animal Organs and the Reversibility of its Power of Decomposing Fats. O. MOHR (*Chem. Centr.*, 1902, ii, 1424; from *Woch. Braü.*, 19, 588—589).—Experiments on the hydrolysis of esters by means of lipase obtained from pig's liver have confirmed Kastle and Loevenhart's conclusions (Abstr., 1901, i, 178) and also strongly support Ostwald's theory of the action of the enzyme. The hydrolysis of the esters is accelerated by the presence of the enzyme, but the action is not complete. If the original solution contained only alcohol and acid, and the enzyme acts as a catalytic agent, then it must be capable not only of causing the decomposition of the ester, but also of promoting its formation from the acid and alcohol. Similar reversible phenomena have been observed in the case of carbohydrate enzymes such as yeast maltase.

E. W. W.

The Function of Peroxides in the Chemistry of the Living Cell. III. Peroxides due to Oxidising Ferments. ROBERT CHODAT and A. BACH (*Ber.*, 1902, **35**, 3943—3947. Compare Abstr., 1902, i, 344, 522).—An oxydase has been obtained from certain fungi,

namely, *Russula fœtens* and *Lactarius vellereus*, which, in addition to exhibiting the ordinary properties of an oxydase, has the property of liberating iodine from acidified potassium iodide solution. The purer the product the more intense is the reaction. The oxydase is stable and is only destroyed by prolonged boiling or addition of mercuric chloride or mineral acids, especially hydrofluoric. Peroxydase has the same action on this oxydase that it has on hydrogen peroxide, namely, rendering it more active. J. J. S.

Hydroxybenzylphosphinic Acid. CHARLES MARIE (*Compt. rend.*, 1902, **135**, 1118—1120).—Two methods have been devised for the production of this acid, which was described by Fossek (Abstr., 1884, 833). By the action of benzaldehyde on a concentrated aqueous solution of hypophosphorous acid, hydroxybenzylhypophosphorous acid, $OH\cdot CHPh\cdot PO_2H_2$, is formed, and when oxidised with bromine gives hydroxybenzylphosphinic acid, $OH\cdot CHPh\cdot PO_3H_2$. This is also obtained by heating benzaldehyde and phosphorous acid together at 100—110° for 20 hours. When heated to 173°, the acid decomposes, but when quickly heated, it melts at 195°. It does not reduce silver salt solutions, but gives a white precipitate of the *silver* salt, $OH\cdot CHPh\cdot PO_3Ag_2$. The *dimethyl ester*, $OH\cdot CHPh\cdot PO_3Me_2$, is produced from the silver salt by the action of methyl iodide, and is very soluble in water, alcohol, or acetone, but only sparingly so in carbon disulphide or ether; it melts at 99°. The *monobenzoyl* derivative, $OBz\cdot CHPh\cdot PO_3H_2$, is obtained from the acid and benzoyl chloride. It is soluble in alcohol, ether, or acetone, sparingly so in benzene, and insoluble in water, melts at 93°, and is very easily saponified. J. McC.

Organo-mercury Compounds of Benzoic Acid. LEONE PESCI (*Gazzetta*, 1902, **32**, ii, 277—296. Compare Abstr., 1900, i, 546; 1901, i, 576 and 624).—The greater part of this paper has been published (*loc. cit.*), the new work being as follows.

The *potassium* ($1\frac{1}{2}H_2O$) and *barium* ($3H_2O$) salts of *o*-chloromercuribenzoic acid are described, and also *potassium* o-*sulphomercuribenzoate* and *potassium, sodium,* and *ammonium* o-*mercuridibenzoates*.

T. H. P.

Organic Chemistry.

Method of Transforming Monochloro- and Monobromo-derivatives of Hydrocarbons into Monoiodo-derivatives. F. Bodroux (*Compt. rend.*, 1902, 135, 1350—1351).—When an ethereal solution of a magnesium alkyl chloride or bromide is treated with powdered iodine in small portions at a time, the alkyl iodide is formed according to the equation: $RMgBr + I_2 = RI + MgBrI$. Using the magnesium compound of propyl bromide or *iso*amyl chloride, an 80 per cent. yield of the corresponding iodo-compound was obtained. The method is applicable also to aromatic derivatives, and works well with the magnesium compound of bromobenzene or *p*-bromotoluene.

J. McC.

Composition and Constitution of Hydrates of Hydrogen Sulphide. Robert de Forcrand (*Compt. rend.*, 1902, 135, 1344—1346. Compare Abstr., 1882, 1027).—The author has previously described a series of mixed hydrates to which he attributed the general formula $M,2H_2S,23H_2O$, M being an easily volatile halogen organic compound, whilst the H_2S may be replaced by H_2Se. From an examination of the dissociation tension of the chloroform compound, it is deduced (compare this vol., ii, 134) that the composition is represented by $CHCl_3,7(\text{or } 8)H_2O + 2(H_2S,6H_2O)$. Further, the conclusion is drawn that chloroform itself must form a simple hydrate, $CHCl_3,7(\text{or } 8)H_2O$; Chancel and Parmentier described a hydrate, $CHCl_3,9H_2O$, which may have been moist. The hydrates previously described contained too much (3 or 4 mols.) water; they are probably all of the type $M,7(\text{or } 8)H_2O + 2(H_2S,6H_2O)$. The 30 halogen organic compounds formerly examined probably all form simple hydrates with $7(\text{or } 8)H_2O$. Methyl chloride gives the hydrate, $CH_3Cl,7H_2O$, and also forms a hydrogen sulphide hydrate.

J. McC.

The Variations in Density of Water-Alcohol Mixtures. H. Vittenet (*Bull. Soc. chim.*, 1903, [iii], 29, 89—92).—The sp. gr. of a series of mixtures of water and alcohol containing less than 10 per cent. of the latter were determined. A Sprengel pycnometer (110 c.c.) was used; it was filled with the mixture, cooled to 0° for 30 minutes, dried, and weighed after a further 15 minutes. The probable errors in the figures given are due (*a*) to the want of sensibility in the balance (±0·000004 gram), (*b*) to the hygrometric state of the atmosphere which invalidates the seventh decimal place, and (*c*) to the reading of the 'meniscus', which is less than 0·0002 gram. The alcohol was prepared by dehydration over baryta, and contained 99·6 per cent. of ethyl alcohol. The following results were obtained:

Alcohol.	Water.	Sp. gr. of mixture.
0·9977	999	0·99980
1·9469	998	0·99961

Alcohol.	Water.	Sp. gr. of mixture.
2·9922	997	0·99941
4·9865	995	0·99904
6·9809	993	0·99865
9·9726	990	0·99807

T. A. H.

Catalytic Oxidation of Alcohols. J. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1903, [iii], 29, 35—47. Compare Abstr., 1901, i, 441, and 496).—The heat of the reaction which ensues when a mixture of air and the vapour of an alcohol impinges on a platinum spiral is usually sufficient to produce and maintain incandescence in the latter. The products formed depend chiefly on the temperature of the spiral, thus, at 200°, methyl alcohol is converted principally into methylal, at a dark red heat, formaldehyde is also formed, whilst at a cherry-red heat these products are replaced by acids, and, at a bright red heat, by carbon dioxide. The investigation has been extended to the following alcohols in addition to those already used (*loc. cit.*), and the conclusions previously arrived at confirmed: ethylene, propylene and phenylene glycols, glycerol, allyl, benzyl, cumyl and cinnamyl alcohols, *iso*eugenol, and saligenin. T. A. H.

Difluoroethyl Alcohol. FRÉDÉRIC SWARTS (*Bull. Acad. Roy. Belg.*, 1902, 11, 731—760. Compare Abstr., 1898, i, 457; 1899, i, 254; 1902, i, 129).—By the action of water and yellow mercuric oxide on difluorobromoethane at 160°, difluoroethyl alcohol, $CHF_2 \cdot CH_2 \cdot OH$, is formed. At temperatures above 180°, the fluorine is eliminated, and solutions of a substance possessing the taste and reducing properties of a sugar are obtained, probably owing to the production and subsequent condensation of glycolaldehyde. Difluoroethyl alcohol, a liquid having an odour resembling that of ethyl alcohol, is miscible with water, being separated from solution by potassium carbonate. It boils at 95·5—96°; solidifies at $-28·2°$; has the sp. gr. 1·31552 at 11·8°, 1·30839 at 17°, 1·2819 at 35·4°, and 1·2199 at 78·4°; and has $n_{H\alpha}$ 1·3345 at 11·8°. The cryoscopic behaviour indicates the existence of a hydrate, $2C_2H_3F_2 \cdot OH,H_2O$, which solidifies at $-39·8°$. The alcohol undergoes association in benzene solution to a less extent than ethyl alcohol, the determination of association in the pure state by the method of Ramsay and Shields leading to a similar conclusion.

Difluoroethyl alcohol possesses more strongly acidic properties than the primary fatty alcohols, forming the sodium and basic calcium and strontium alkoxides by the action of the hydroxide or oxide of the metal at the ordinary temperature, a similar reaction ensuing with potassium carbonate, but not with the hydrogen carbonate. The *acetate* forms a colourless liquid boiling at 106° and having a sp. gr. 1·1781 at 15°; its saponification constant is almost exactly equal to that of phenyl acetate.

The alcohol attacks glass at high temperatures, but ammoniacal silver nitrate is not reduced by it. On oxidation, difluoroacetic acid is formed, all attempts to prepare the aldehyde having so far proved

unsuccessful. *Difluoroethyl chloride*, prepared in small quantities by the action of phosphorus pentachloride, is a liquid, heavier than water, boiling at 36°. G. D. L.

Acetol (Acetylcarbinol) and its Reduction Products. ANDRÉ KLING (*Bull. Soc. chim.*, 1903, [iii], **29**, 92—96).—Acetylcarbinol, when reduced in alkaline solution by sodium amalgam, furnishes a mixture of propylene glycol and *iso*propyl alcohol; when the reduction is effected in neutral or acid solution, acetone and propylene glycol are produced (compare Perkin, Trans., 1891, **59**, 790). These reactions are, the authors consider, inexplicable by the formula $CH_2Ac{\cdot}OH$, usually assigned to acetylcarbinol, and they prefer to regard this substance as consisting, at least partially, of the tautomeric substance $O{<}\begin{matrix}CMe{\cdot}OH\\ |\\ CH_2\end{matrix}$. T. A. H.

Contraction on Mixing Chloroform with Ethyl Ether. A. N. GEORGIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, ii, 565—572).—The author has determined, at temperatures between 20° and 22°, the percentage contractions occurring when chloroform and ether are mixed in varying proportions. The coefficient of contraction increases with the proportion of either liquid present up to a maximum of 1·4 per cent., which corresponds approximately with a liquid of the composition $CHCl_3,Et_2O$. T. H. P.

Methyl Dinitroethyl Ether. JAKOB MEISENHEIMER (*Ber.*, 1903, **36**, 434—438).—The *potassium* salt, $OMe{\cdot}CH_2{\cdot}C(NO_2){:}NO{\cdot}OK$, of methyl dinitroethyl ether, obtained by the interaction in methyl alcoholic solution of potassium hydroxide and trinitroethane at the ordinary temperature, crystallises in bright yellow needles and decomposes at 162°; with dilute sulphuric acid, it gives *methyl dinitroethyl ether*, $OMe{\cdot}CH_2{\cdot}CH(NO_2)_2$, boiling at 84° under 7 mm. pressure, and, with bromine water, *methyl bromodinitroethyl ether*,

$$OMe{\cdot}CH_2{\cdot}CBr(NO_2)_2,$$

which boils at 84° under 7 mm. pressure. The latter, by the action of methyl-alcoholic potassium iodide, is reconverted into the potassium salt of methyl dinitroethyl ether, iodine being quantitatively liberated.

Hantzsch and Rinckenberger's "dinitroethane alcoholate" (Abstr., 1899, i, 404) is really dinitroethyl ether, $OEt{\cdot}CH_2{\cdot}CH(NO_2)_2$, analogous to the methyl ether described above; this the author considers is proved by the fact that nitrous acid in practically theoretical quantity, and not ethyl nitrate, is formed in its production, and by the analyses given in the present paper, which do not agree with a formula containing two additional hydrogen atoms as required by Hantzsch's hypothesis. W. A. D.

Chloroethyl Nitrite. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1902, **11**, 713—721).—Chloroethyl nitrite, prepared by the addition of hydrochloric acid to an aqueous solution of chloroethyl alcohol and

sodium nitrite in mol. proportions, boils at 95—96° under atmospheric pressure, and not at 117° as stated by Bertoni, and has a sp. gr. 1·221 at 20°. Ethyl nitrite is formed quantitatively on gently warming chloroethyl nitrite with an excess of ethyl alcohol; with acetyl chloride in the cold, chloroethyl acetate and nitrosyl chloride are formed.

The boiling point observed by the author is in harmony with that of α-chloropropyl nitrite (105—106°), and is in conformity with the boiling point relationships of the ethane and propane series, some details of which are given in the paper. G. D. L.

Constitution of Platinum Bases. PETER KLASON (*J. pr. Chem.*, 1903, [ii], 67, 1—40. Compare Abstr., 1895, ii, 400, and Jörgenson, Abstr., 1900, i, 542).—*Platosemiammine chloride*, formed from its potassium salt by the action of platinum chloride, is a crystalline, yellowish-brown powder, which is only slightly soluble in cold, and is hydrolysed by hot, water. The action of mercaptan on ammonium platosemiammine chloride leads to the formation of a *substance* having the formula $4SEt\cdot Pt\cdot NH_3Cl,PtCl\cdot NH_3Cl$, which, when boiled with hydrochloric acid, yields *platosemichloridesemimercaptide*, $SEt\cdot PtCl$; this, with ammonia, yields a brownish-yellow, amorphous *polymeride* of platosemimercaptidesemiammine chloride, $SEt\cdot Pt\cdot NH_3Cl$.

Platosemiamminemercaptide, $SEt\cdot Pt\cdot NH_3\cdot SEt$, formed by the action of 2 mols. of mercaptan on ammonium platosemiammine chloride, is very unstable.

Platosemimercaptidesemidiammine chloride, $NH_3{:}Pt(SEt)\cdot NH_3Cl$, formed by the action of ammonia on the corresponding ethylsulphine compound, is monobasic, and yields, on addition of hydrochloric acid and potassium iodide, *platosemimercaptidesemiammine iodide*, $SEt\cdot Pt\cdot NH_3I$, which is insoluble, and at 130° forms platosemichloridesemimercaptide platosemimercaptidesemiammine chloride, $SEt\cdot PtCl,Pt(SEt)\cdot NH_3Cl$, which is a crystalline, yellow powder.

Platosemimercaptidesemi-iodide, $Pt(SEt)I$, formed from the semiammine iodide at 175°, is a red, crystalline powder. *Platosemimercaptidesemidiammine iodide*, $NH_3{:}Pt(SEt)\cdot NH_3I$, crystallises in white needles. The action of mercaptan on α-platodiammonia chloride, $NH_3{:}Pt(NH_3\cdot Cl)Cl$, leads to the formation of platosemimercaptidesemidiammine chloride.

Platoammine hydroxide, $Pt(NH_3\cdot OH)_2,2H_2O$, formed by the action of baryta on the sulphate, crystallises in needles, is easily soluble, and has an alkaline reaction. With phenylmercaptan, it yields the *phenylmercaptide*, $Pt(NH_3\cdot SPh)_2$, which crystallises in clusters of yellow needles and is insoluble in water and only slightly so in alcohol. The *ethylmercaptide* is soluble in water and easily loses ammonia.

When treated with mercaptan, β-platodiammonia chloride yields platosemiamminemercaptidesemiammine chloride,

$$SEt\cdot NH_3\cdot Pt\cdot NH_3Cl.$$

When warmed with hydrochloric acid, platosemiamminesemidiammine chloride yields β-platodiammine chloride and not the α-isomeride (compare Jörgenson). In aqueous solution, platosemidiamminesemiethylsulphineammine chloride loses ammonia and forms the *semi-*

ammine, $SEt_2{:}Pt(NH_3Cl)_2$, which crystallises in colourless prisms and loses ethyl sulphide at 100°. The *double* salt,

$$NH_3{:}Pt({:}SEt_2)(NH_3Cl)_2,PtCl_2,$$

crystallises in rose-coloured, rhombic leaflets, and easily decomposes, losing ethyl sulphide. The *double* salt, $SEt_2{:}Pt(NH_3Cl)_2,PtCl_2$, crystallises in short, green prisms, and is slowly decomposed by water.

The *mercaptide*, $SEt_2{:}Pt(NH_3{\cdot}SEt){\cdot}NH_3Cl$, formed by the action of mercaptan on the corresponding chloride, decomposes, when dried, into ethyl sulphide and platosemiamminemercaptidesemiammine chloride. *Platopyridinephenylmercaptide*, $Pt(C_5NH_5{\cdot}SPh)_2$, resembles the corresponding ammine, and loses pyridine at 120°.

The action of alcoholic ammonia on α- or β-platodimethylsulphine chloride leads to the formation of *platoamminemethylsulphine chloride*, $Pt({:}NH_3)_2(SMe_2Cl)_2$, which crystallises in white prisms, with potassium iodide yields ammonia and *platodimethylsulphine iodide*, and changes in solution into platosemidiamminesemimethylsulphineammine chloride, $NH_3(SMe_2)Pt(NH_3Cl)_2$. G. Y.

Theory of the Process of Saponification. JULIUS LEWKOWITSCH (*Ber.*, 1903, 36, 175—176).—The views on the process of saponification put forward by Balbiano (Abstr., 1902, i, 450) are criticised, more especially as regards the statement that glycerol is not found to be present if hydrolysis is stopped before the glyceride is completely decomposed. K. J. P. O.

Ethyl Dinitroacetate. LOUIS BOUVEAULT and ANDRÉ R. WAHL (*Compt. rend.*, 1903, 136, 159—160).—When 1 part of ethyl hydrogen malonate is slowly added to 3 parts of fuming nitric acid, the temperature kept below 30°, and finally the mixture poured on to ice, a heavy oil is formed; the product is dissolved in sodium carbonate solution, and a mineral acid added, when *ethyl dinitroacetate*, $CH(NO_2)_2{\cdot}CO_2Et$, is precipitated as an oil. It has a sp. gr. 1·369 at 0°, is slightly soluble in water, to which it imparts a yellow colour, has strong acid properties, and decomposes carbonates; its alkali derivatives are not decomposed by acetic or oxalic acid. The *potassium* derivative, $CK(NO_2)_2{\cdot}CO_2Et$, crystallises in long, yellow needles, and dissolves in water to a yellow solution from which mineral acids precipitate the ester as a colourless oil. The *ammonium* derivative produced by passing ammonia into a hot solution of the ester in a mixture of methyl alcohol and benzene forms sulphur-yellow needles.

Ethyl dinitroacetate is also produced by nitrating substituted acrylic esters. J. McC.

Synthetically Prepared Simple and Mixed Glycerides of the Fatty Acids. FERDINAND GUTH (*Zeit. Biol.*, 1902, 44, 78—110).—Animal and vegetable fats are now generally considered to be, not only mixtures of tristearin, tripalmitin, and triolein, but also mixed glycerides of the fatty acids (compare Hansen, Abstr., 1902, i, 339). A large number of mono- and di-glycerides and of mixed glycerides have been prepared in order to compare them with the natural fats.

α-Monostearin, $C_2H_3(OH)_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35}$, prepared by heating

equivalent quantities of an α-monochlorohydrin and sodium stearate at 110° for four hours, crystallises in plates from methyl alcohol, melts at 73° and boils at 260° under 12 mm. pressure with partial decomposition; for this substance, Berthelot (*Chimie organique fondée sur la synthese*) and Hundeshagen (Abstr., 1884, 220) have given the melting point 61—62°. αγ-Distearin, prepared by heating αγ-dichlorohydrin and sodium stearate at 140—150° for 6—8 hours, crystallises in rhombic leaflets melting at 72·5°. αβ-Distearin, prepared from αβ-dibromohydrin and sodium stearate, crystallises in prismatic plates melting at 74·5°; Berthelot (*loc. cit.*) prepared a distearin from glycerol and stearic acid which melted at 58°, and Hundeshagen, one melting at 76·5°. Tristearin was prepared by heating αβγ-tribromopropane and sodium stearate for 10 hours at 170—180°, or by heating equal quantities of αγ-distearin and stearic acid at 200—220° under diminished pressure; it was identical in all its properties with the tristearin previously described.

α-Monopalmitin, prepared from the chlorohydrin, crystallises in plates melting at 65°; Berthelot (*loc. cit.*) gives the melting point 58°, and Chittenden and Smith (Abstr., 1885, 508) give 63°. αγ-Dipalmitin crystallises in groups of needles melting at 69°; αβ-dipalmitin forms leaflets melting at 67°; the dipalmitins of Berthelot and Chittenden and Smith melted respectively at 59° and 61°. Tripalmitin, prepared from αβγ-tribromopropane and sodium stearate and from dipalmitin and palmitic acid, crystallises in needles and melts at 65·5°.

α-Mono-olein, prepared by heating α-chlorohydrin with excess of sodium oleate at 140° in an atmosphere of carbon dioxide, is an oil which solidifies at 0° and boils with decomposition at about 300° under 15 mm. pressure. αγ-Diolein, prepared in a similar manner from dichlorohydrin, solidifies at 0°. αβ-Diolein, prepared from dibromohydrin, is an oil. Triolein, prepared from αβγ-tribromopropane, solidifies at −5° to −4°, and boils at 235—240° under 18 mm. pressure.

α-Monobutyrin, prepared from chlorohydrin, boils at 269—271° under the atmospheric and at 160—163° under 16 mm. pressure. αγ-Dibutyrin boils at 173—176° under 19 mm. and at 279—282° under the ordinary pressure. αβ-Dibutyrin boils at 166—168° under 19 mm., and at 273—275° under the ordinary pressure. Tributyrin, prepared from dibutyrin and butyric acid, boils at 182—184° under 24 mm. and at 287—288° under the ordinary pressure.

*α-Mono*iso*butyrin*, prepared from chlorohydrin and sodium *iso*butyrate, is an oil boiling at 158—161° under 19 mm. and at 264—266° under the ordinary pressure. *αγ-Di*iso*butyrin* boils at 164—167° under 22 mm. and at 272—275° under the ordinary pressure; *αβ-di*iso*butyrin* boils at 159—162° under 20 mm. and at 269—272° under the ordinary pressure; *tri*iso*butyrin* boils at 173—176° under 24 mm. and at 282—284° under the ordinary pressure.

α-Stearyldipalmitin, prepared by heating monostearin and palmitic acid under diminished pressure, crystallises in rhombic plates melting at 60°; *β-stearyldipalmitin*, prepared from αγ-dipalmitin and stearic acid, forms leaflets melting at 60°; Hansen (*loc. cit.*) has obtained two stearyldipalmitins, both melting at 55°, from mutton tallow.

a-Palmityldistearin, prepared from *a*-monopalmitin and stearic acid, forms leaflets melting at 63°; Hansen's material, prepared from mutton tallow, melted at 62·5°.

β-Acetyldibutyrin, $OAc \cdot CH(CH_2 \cdot O \cdot COPr^{a})_2$, prepared from acetyldichlorohydrin and sodium butyrate, or from *αγ*-dibutyrin and acetyl chloride, is a colourless oil boiling at 173—175° under 16 mm. and at 289—291° under the ordinary pressure. *β-Benzoyldibutyrin*, prepared from benzoyldichlorohydrin and sodium butyrate, is a colourless oil boiling at 230—233° under 18 mm. pressure. *β-Benzoyldistearin*, prepared from benzoyldichlorohydrin and sodium stearate, forms crystals melting at 64°. *β-Acetyldibenzoin*, prepared from acetyldichlorohydrin and sodium benzoate, is a thick, colourless oil boiling at 248—251° under 22 mm. pressure. *β-Benzoyldichlorohydrin*, $(CH_2Cl)_2 \cdot CH \cdot COBz$, prepared from *αγ*-dichlorohydrin and benzoyl chloride, is an oil boiling at 171—173° under 19 mm. and at 296° with slight decomposition under the ordinary pressure.

The double melting point of triglycerides has been examined, more especially in the case of tristearin; this glyceride melts at 71·5° and then solidifies to a material melting at 55°, but solidifying above that temperature, to melt again at 71·5°. It is thought that the material which has melted and again solidified is in an amorphous and labile condition; on heating, this passes over into the stable and crystalline form with so much evolution of heat that the substance melts; hence the apparent melting point at 55°. It has been experimentally ascertained that at the apparent melting point, at 55°, a development of heat occurs (compare Hansen, *loc. cit.*).

K. J. P. O.

Isomerism between Oleic and Elaidic Acids and Erucic and Brassidic Acids. II. Alexius Albitzky (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 788—810. Compare Abstr., 1899, i, 862).—It has been shown previously (*loc. cit.*) by the author that by the successive action of hydrochloric acid and potassium hydroxide on oleic, elaidic, erucic, and brassidic acids, dihydroxy-acids are obtained which are not identical with, but stereoisomerides of, those yielded by the same unsaturated acids when oxidised with potassium permanganate. In the present paper, it is shown that there are other reactions of these acids which yield abnormal, that is, geometrically isomeric, products; by working under different conditions, any one of the above unsaturated acids may be made to yield whichever of two dihydroxy-acids may be desired. Further, each of the dihydroxy-acids may be converted into its stereoisomeride or into an unsaturated acid belonging to the other stereoisomeric series.

From the results of the former experiments (*loc. cit.*) and of those described below, it is concluded that it is not always possible, from the known configuration of the initial compound, to judge of the configuration of the products it yields.

Thus, when the dihydroxystearic acid melting at 136·5° is acted on by hydrogen bromide, it is converted into two dibromostearic acids, identical respectively with the acids formed by the action of bromine

on oleic and elaidic acids; the latter acids are obtained on treating the dibromo-acids with zinc and hydrochloric acid.

By treating the dihydroxystearic acid melting at 133—135° with acetic acid and hydrogen bromide, the acetyl derivative of bromohydroxystearic acid is obtained, and on hydrolysing this with potassium hydroxide and treating the product with dilute hydrochloric acid, the stereoisomeric dihydroxystearic acid melting at 95—97° is obtained. The same acid is arrived at if the bromoacetoxystearic acid is treated with barium hydroxide and the product with dilute sulphuric acid.

In the same way, the dihydroxybehenic acid melting at 99° may be converted into bromoacetoxybehenic acid, which can then be transformed either into the stereoisomeric dihydroxybehenic acid melting at 130—132° or, by the successive action of barium hydroxide and hydrochloric acid, into glycidic acid.

On converting the bromoacetoxystearic acid prepared from the dihydroxystearic acid of high melting point into its diacetyl derivative and hydrolysing this with barium hydroxide, a mixture of the two dihydroxystearic acids is obtained, that with the higher melting point largely preponderating. The axially-symmetrical dihydroxystearic acid is thus converted into the plane-symmetrical bromoacetoxystearic acid, which then yields axially-symmetrical diacetoxystearic acid.

Stereoisomeric change also takes place when the dihydroxystearic acid of high melting point is converted directly into its diacetyl derivative.

If the dibromide of erucic acid is fused with silver oxide, it yields only one dihydroxybehenic acid, and, under the same conditions, oleic acid dibromide gives one dihydroxystearic acid. On the other hand, however, the dibromide of erucic acid yields two diacetyl derivatives of the dihydroxybehenic acids. Similarly, elaidic acid dibromide gives rise to the two stereoisomeric dihydroxystearic acids, and brassidic acid dibromide to the two dihydroxybehenic acids. T. H. P.

Oxidation of Unsaturated Acids by Caro's Reagent. ALEXIUS ALBITZKY (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 810—828).—On oxidation with Caro's acid, elaidic acid yields the dihydroxystearic acid melting at 129—132°, obtained by the oxidation of oleic acid. In the same way, oleic acid yields the dihydroxystearic acid melting at 95—98·5°, formed by oxidising elaidic acid with potassium permanganate; erucic acid gives the dihydroxybehenic acid obtained when brassidic acid is oxidised by potassium permanganate, and brassidic acid gives the same dihydroxybehenic acid as is yielded by erucic acid when oxidised with permanganate.

In the oxidation of elaidic acid by Caro's acid, the formation of an intermediate product of the composition $C_{18}H_{34}O_2,H_2SO_5$ was detected. The oxidation therefore takes place in two stages. With oleic acid, H_2SO_5 is first added on, giving a compound,

$$C_8H_{17}\cdot CH(OH)\cdot CH(O\cdot SO_2\cdot OH)\cdot[CH_2]_7\cdot CO_2H,$$

which, under the action of water, yields dihydroxystearic acid, $C_8H_{17}\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H$. T. H. P.

$\beta\delta$-Dimethylsorbic Acid. I. HANS RUPE and WALTHER LOTZ (*Ber.*, 1903, 36, 15—16).—*Ethyl $\beta\delta$-dimethylsorbate*,
$CMe_2{:}CH{\cdot}CMe{:}CH{\cdot}CO_2Et$,
prepared by the action of zinc on a mixture of mesityl oxide and ethyl bromoacetate, boils at 94° under 14 mm. pressure; *$\beta\delta$-dimethylsorbic acid*, obtained by hydrolysing the ester with dilute aqueous alcoholic sodium hydroxide, crystallises from dilute alcohol in slender, white needles or, on slow evaporation, in large plates, and melts at 93°. On reduction with sodium amalgam, *$\beta\delta$-dimethyldihydrosorbic acid* is obtained as a colourless oil boiling at 115—117° under 11·5 mm. and at 119—120° under 14 mm. pressure. W. A. D.

Acetylglycollic Acid. RICHARD ANSCHÜTZ and W. BERTRAM (*Ber.*, 1903, 36, 466—468).—*Acetylglycollic acid*, $OAc{\cdot}CH_2{\cdot}CO_2H$, which can be readily prepared by gently heating glycollic acid with acetyl chloride, crystallises in needles, melts at 66—68°, and boils at 144—145° under 12 mm. pressure. The *chloride*, $OAc{\cdot}CH_2{\cdot}COCl$, is obtained by the action of phosphorus trichloride on acetylglycollic acid and is a refractive liquid which boils at 54° under 14 mm. pressure, has the sp. gr. 1·2675, and is decomposed by water and the alcohols. The *amide*, $OAc{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, crystallises in slender needles and melts at 93—95°.

Acetyllactic acid boils at 127° under 11 mm. pressure, and its *chloride* at 56° under 11 mm. pressure. A. H.

New Synthesis of Camphocarboxylic Acid. NICOLAI ZELINSKY (*Ber.*, 1903, 36, 208—209. Compare Baubigny, *Ann. Chim. phys.*, 1870, [iv], 19, 255; Brühl, Abstr., 1892, 201).—Bromocamphor (m. p. 76°) is dissolved in ether, treated with a tenth of its weight of pure dry magnesium powder, and then with carbon dioxide. The resulting compound is decomposed with water and dilute sulphuric acid, the ethereal solution extracted with potassium hydroxide, and the alkaline extract acidified. The yield is about 50 per cent.
J. J. S.

Complex Platinum Salts. VI. Platoso oxalonitrous Acid and Salts. MAURICE VEZÉS (*Bull. Soc. chim.*, 1903, [iii], 29, 83—87. Compare Abstr., 1901, i, 187, and this vol., ii, 25).—*Sodium platoso-oxalonitrite*, $Pt(C_2O_4)(NO_2)_2Na_2,H_2O$, prepared by double decomposition between the barium salt and sodium sulphate, forms yellow, triclinic crystals [$a:b:c = 0{\cdot}68153:1:0{\cdot}94068$; $\alpha = 89°48'40''$, $\beta = 91°41'45''$, $\gamma = 97°6'20''$], is soluble in its own weight of boiling, and in four times its weight of cold, water. The hydrated crystals are stable in air, are slowly dehydrated at 100°, but more rapidly at 150—200°. At 270°, the salt is decomposed, forming metallic platinum, sodium nitrite, and carbon dioxide. The *ammonium* salt, produced in a similar manner, is only stable in solution. *Platoso-oxalonitrous acid*, a solution of which is produced by the addition of sufficient dilute sulphuric acid to a solution of the barium salt, decomposes with the formation of an uncrystallisable blue syrup when the solution is evaporated, even under

reduced pressure, at the ordinary temperature. When cupric sulphate is added to a solution of the barium salt, a mixture of barium sulphate and copper oxalate is precipitated, whilst various decomposition products remain in solution, including probably Nilson's triplatoso-octonitrous acid. It appears, therefore, that the platoso-oxalonitrites of the heavy metals are incapable of existence in aqueous solution.

T. A. H.

The Acidic Properties of Ethyl Malonate. Daniel Vorländer [and, in part, with Erich Mumme, P. Groebel, and K. Tubandt] (*Ber.*, 1903, **36**, 268—281. Compare Vorländer and Schilling, Abstr., 1899, i, 672).—The sodium derivatives of ethyl malonate are regarded as C-derivatives of the type $CHNa(CO_2Et)_2$, and not as O-derivatives such as $ONa\cdot C(OEt)\colon CH\cdot CO_2Et$. Numerous arguments and observations are brought forward in support of this view.

Ethyl sodiomalonate is not stable in the presence of water, as it should be if the metal were attached to oxygen as in the grouping $O\colon C\cdot CH\colon C\cdot ONa$. The ester yields no coloration with ferric chloride.

Ebullioscopic determinations of mixtures of ethyl benzoate and sodium ethoxide in absolute alcoholic solution indicate that practically no additive product is present in the boiling solution (compare Claisen, *Ber.*, 1887, **20**, 649). The results previously obtained by Vorländer and Schilling with mixed solutions of ethyl malonate and sodium ethoxide can thus only be explained by the assumption that a certain amount of ethyl sodiomalonate is present in the solution.

An absolute alcoholic solution of benzylideneacetone is readily coloured by sodium methoxide solution; benzyl cyanide and ethyl phenylacetate do not interfere with this coloration, whereas ethyl malonate and ethyl acetoacetate prevent the development of the coloration to a certain extent, owing to the formation of sodio-derivatives.

Aqueous solutions of ethyl malonate are electrolytes, the dissociation constant K has a value about 0·0000015; in absolute alcohol, the conductivity of the ester is no greater than that of ethyl benzoate in the same solvent.

The presence of ethyl malonate reduces, to a considerable extent, the conductivity of alcoholic solutions of sodium methoxide. The reaction is evidently of the type: ethyl malonate + sodium methoxide $\rightleftarrows$ ethyl sodiomalonate + methyl alcohol. Ethyl benzoate has no effect on the conductivity of solutions of sodium methoxide.

The inversion of *l*-menthone (Beckmann, Abstr., 1889, 721) under the influence of sodium ethoxide has been studied, both with and without the addition of ethyl malonate, by the aid of the equation: $dx/dt = K(a-x) - K'(a'+x)$. The following values for $K+K'$ have been obtained: 1 mol. sodium ethoxide, 0·019; 1 mol. sodium ethoxide + 1 mol. ethyl malonate, 0·0082; 1 mol. sodium ethoxide + 2 mols. ethyl malonate, 0·0050; 1 mol. sodium ethoxide + 4 mols. ethyl malonate, 0·0034. If ethyl sodiomalonate itself has no inverting

action, it follows, from the numbers obtained, that at 20°, and with a concentration of 0·654 gram per 100 c.c., about 35 per cent. of the sodio-derivative is converted into ethyl malonate and sodium ethoxide under the influence of the alcohol.

Ethyl phenylacetate, ethyl benzoate, and sodium acetate do not affect the inverting power of sodium ethoxide.

In order to compare the acidic properties of ethyl malonate with those of other feeble acids, experiments have been made by taking 100 c.c. of solution containing 10 grams of *l*-menthone, 1/500 gram-mol. of sodium ethoxide, and 1/500 gram-mol. of the acid, and comparing the values obtained for $K+K'$. Ethyl malonate and ethyl aconitate give practically the same value, namely, 0·0055 and 0·0051. Ethyl acetoacetate gives a much lower value, 0·00017, and phenol an intermediate value, 0·0008. Ethyl cyanoacetate gives the value 0·00095, and acetic acid reduces the number to practically nil. Ethyl phenylacetate, triphenylmethane, benzyl alcohol, and water do not affect the number, indicating that they do not react with the sodium ethoxide. J. J. S.

Preparation of Teraconic Acid. HANS STOBBE (*Ber.*, 1903, 36, 197—199).—A reply to Petkow (this vol., i, 147). Good yields of teraconic acid may be obtained by mixing together acetone, b. p. 56—58°, ethyl succinate, and sodium ethoxide in the presence of ether and leaving the mixture for several days in a freezing mixture. The mixed sodium salts are thoroughly extracted with ether and then acidified with a large excess of 30—50 per cent. sulphuric acid, when the greater part of the teraconic acid separates in the form of colourless needles. The acid esters may be hydrolysed with baryta.

J. J. S.

Decomposition of some Di- and Tri-basic Organic Acids. WILLIAM ŒCHSNER DE CONINCK and RAYNAUD (*Compt. rend.*, 1902, 135, 1351—1352).—Malonic acid, when heated with ethylene glycol or with glycerol, gives carbon dioxide and a dilute solution of acetic acid. When succinic acid is heated with glycerol, no gas is evolved, but acraldehyde and acrylic acid are produced. Succinic acid and sulphuric acid, when heated, form a homogeneous solution. *d*-Tartaric acid and glycerol, when heated, give off large volumes of carbon dioxide; at the same time, acraldehyde and a combustible gas which is not absorbed by bromine at the ordinary temperature are produced. *d*-Tartaric acid dissolves in ethylene glycol, and when the solution is heated a small quantity of carbon dioxide is evolved. With sulphuric acid, it gives carbon dioxide, carbon monoxide, and methane. Malic acid, when heated with glycerol, decomposes giving carbon dioxide and acraldehyde; with sulphuric acid, it gives carbon dioxide and a large quantity of carbon monoxide. Where the acids are heated in a sealed tube, some methane is also produced. When citric acid is heated with glycerol, carbon dioxide, a little carbon monoxide, and methane are produced. Malonic acid and sulphuric acid, when heated together, give carbon dioxide and acetic acid. J. McC.

Polymerides of Formaldehyde. MARCEL DESCUDÉ (*Bull. Soc. chim*, 1903, [iii], 29, 87—89. Compare Abstr., 1902, i, 738).—Four specimens of formaldehyde polymerides obtained (*a*) by polymerisation of the aldehyde with sulphuric acid, (*b*) by evaporating to dryness below 100° a 40 per cent. aqueous solution of the aldehyde, (*c*) by similar treatment of a 15 per cent. aqueous solution of a "soluble" commercial trioxymethylene, and (*d*) by purchase, were examined as regards solubility in water, volatility, reactivity with acetyl chloride, and percentage of carbon.

Two grams of each of the specimens *a*, *b*, *c*, and *d* lost, when kept in a vacuum over sulphuric acid at the ordinary temperatures, respectively, 0, 0·006, 0·053, and 0·067 gram per day (24 hours). Their solubilities in water and reactivities with acetyl chloride increase from *a* to *d*, whilst the amount of carbon contained decreases in the same order. These differences have also been observed in the commercial "trioxymethylenes" of different makers, and are to be ascribed not to the existence of hydrates of the type $(CH_2O)_n,H_2O$, as suggested by Lösekann (Abstr., 1892, 423), but to the existence of several physical modifications of formaldehyde polymerides (or mixtures of these) analogous to the red and yellow mercuric oxides (compare Tollens and Mayer, Abstr., 1888, 809). T. A. H.

Ignition of Gun-cotton by means of Water. LUDWIG VANINO (*Zeit. angew. Chem.*, 1902, 15, 1299—1300).—Sodium peroxide can be mixed with dry gun-cotton without causing ignition. If water be added to the mixture, it immediately catches fire. A solution of formaldehyde is still more efficacious. K. J. P. O.

Discrimination between Aminic and Acidic Functions by means of Formaldehyde. HUGO SCHIFF (*Annalen*, 1902, 325, 348—354. Compare Abstr., 1902, i, 85, 250).—The discrimination between basic and acid functions in amino-acids by means of formaldehyde is the less complete the more dilute the solution. With the salts formed by ammonia or alkylamines with mineral acids, dilution has little influence.

Comparative experiments made with litmus and phenolphthalein show, in the case of ammonia and alkylamine salts, results which often deviate to a large extent accordingly as the compounds formed after the addition of formaldehyde have basic properties or not. For example, ethylamine hydrochloride and formaldehyde give a solution in which the whole of the acid can be titrated with potassium hydroxide in the presence of phenolphthalein, but only half in the presence of litmus. Hydrazine salts behave in a very characteristic manner; when titrated in the presence of litmus with potassium hydroxide, exactly half the acid is neutralised; if now formaldehyde is added, the other half of the acid can be titrated; in the phenolphthalein, on the other hand, considerably more than half the acid can be titrated before the addition of formaldehyde, and the remainder after the aldehyde is added. With both indicators, the total titre is the same. K. J. P. O.

Monocarbon Derivatives. XIV. Action of Ammonia on Formaldehyde. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1902, 11, 721—729).—By the action in the cold of ammonia (1 mol.) on formaldehyde (1 mol.) in 40 per cent. solution, trihydroxytrimethylamine, $N(CH_2\cdot OH)_3$, is formed as a faintly coloured liquid, of ammoniacal odour and bitter taste, soluble in water and alcohol, insoluble in chloroform, ether, and methyl formate, and having a sp. gr. 1·025 at 17·5°. By the action of water, by prolonged desiccation, or by spontaneous evaporation, the compound passes into liquid mixtures probably containing mono-, di-, and tri-hydroxymethylamines, hexamethylenetetramine being finally produced by condensation of hydroxymethylamine with trihydroxytrimethylamine. A mixture of the two latter bases is formed by the action of water on the tetra-amine.

G. D. L.

Double Salt of Silver Iodide. D. STRÖMHOLM (*Ber.*, 1903, 36, 142—143).—When half an equivalent of silver nitrate is added to a solution of tetraethylammonium iodide, a *double* salt, $NEt_4I,2AgI$, is precipitated, which is of a pure white colour, and is not affected by daylight. When heated, it sinters above 215° and melts at 225—230°, and at a higher temperature decomposes, leaving a residue of pure silver iodide. The salt is only stable in solution in the presence of a small excess of the tetraethylammonium iodide, and is at once decomposed by silver nitrate.

A. H.

Formaldehyde Derivatives of Aliphatic Bases. CARL A. BISCHOFF and F. REINFELD (*Ber.*, 1903, 36, 35—40).—Definite products from the interaction of formaldehyde with trimethylenediamine and with tetramethylenediamine could not be isolated. Pentamethylenediamine (cadaverine) gives, principally, an insoluble, amorphous *base*, $(CH_2{:}N\cdot[CH_2]_5\cdot N{:}CH_2)_n$, which becomes yellow at 200°, sinters at 235°, and melts in a closed tube at 251°; it is opaque, but becomes transparent on moistening with various solvents, and on heating gelatinises and then dissolves. It is soluble in dilute mineral acids, and is so stable that when heated for 4 hours with dilute hydrochloric acid or aqueous sodium hydroxide it does not lose formaldehyde. Unlike the salts of cadaverine, the salts of this base are poisonous.

Formaldehyde condenses with urethane at the ordinary temperature, giving only a small proportion of a definite product, namely, *anhydroformaldehydeurethane*, $CO_2Et\cdot N{<}{}^{CH_2}_{CH_2}{>}N\cdot CO_2Et$, which forms large prisms, melts at 100°, and boils at 186—190° under 20 mm. pressure.

W. A. D.

Synthesis of *d*-Glucosamine. EMIL FISCHER and HERMANN LEUCHS (*Ber.*, 1903, 36, 24—29).—*d*-*Arabinosimine*, obtained by the addition of ammonia to *d*-arabinose, is converted by hydrogen cyanide into *d*-glucosamic acid (compare this vol., i, 12), identical with the natural product in solubility and specific rotatory power. On reducing the hydrochloride of the derived lactone with sodium amalgam, *d*-glucos-

amine is formed, and can be isolated in the form of its phenylcarbimide derivative (Steudel, Abstr., 1902, i, 399).

These facts indicate that the configuration of *d*-glucosamine is that of dextrose or *d*-mannose, in which the α-hydroxyl is replaced by amidogen, the stereochemical position of this group being still undetermined.

W. A. D.

Ethyl β-Aminocrotonate and Nitrous Acid. HANS EULER (*Ber.*, 1903, **36**, 388—392).—Ethyl β-aminocrotonate,

$$CH_3\cdot C(NH_2)\colon CH\cdot CO_2Et,$$

can be estimated in presence of ethyl acetoacetate by a method similar to the thiocyanate method of estimating silver; a standard ferric solution is run in from a burette until the whole of the amino-ester is decomposed, the iron hydroxide produced being precipitated in a flocculent form; after this, the violet ferric salt of ethyl acetoacetate begins to separate, and the solution becomes colloidal and turbid. Using this method, it was found that, when dissolved in water, the amino-ester is decomposed to the extent of 50 per cent. in 60 hours, but that acids, including acetic acid, cause an immediate and quantitative decomposition. This decomposition is also brought about by nitrous acid, the products being ammonium nitrite (or nitrogen) and ethyl acetoacetate or its *iso*nitroso-derivative (compare Collie, Abstr., 1885, 373).

T. M. L.

$\beta\gamma$-Diaminoadipic Acid and a New Method of Preparing γ-Amino-acids. WILHELM KÖHL (*Ber.*, 1903, **36**, 172—174).—When muconic acid is heated with concentrated ammonia at 135—140°, the double lactam of $\beta\gamma$-diaminoadipic acid is formed; this substance, which has recently been prepared by Traube (this vol., i, 76), melts at 275° and forms a *hydrochloride* which crystallises with H_2O. A far better yield of $\beta\gamma$-diaminoadipic acid is obtained by heating muconamide (Ruhemann, Trans., 1890, **57**, 372) with concentrated ammonia at 150° for 5 hours.

γ-Amino-acids can be obtained from the amides of $\Delta^{\beta\gamma}$-unsaturated acids. Thus the amide of phenyl*iso*crotonic acid yields γ-aminophenylbutyric acid. *Phenyl*iso*crotonamide*, prepared by shaking the corresponding ester with concentrated ammonia, crystallises in leaflets melting at 130°; when the amide is heated under pressure at 160°, γ-aminophenylbutyric acid is obtained, and crystallises in scales melting and decomposing at 216°; it yields a *hydrochloride* crystallising in prisms melting and decomposing at 180°. Together with the amino-acid, a *substance* is obtained which crystallises in flattened needles melting at 91°, and is probably the lactam. K. J. P. O.

Ammonium Salts as the Simplest Ammonio-metallic Compounds. ALFRED WERNER (*Ber.*, 1903, **36**, 147—159. Compare Abstr., 1893, ii, 379; 1902, ii, 554).—Ammonio-metallic compounds may be regarded as being formed from ammonia and metallic salts just as ammonium chloride is produced from ammonia and hydrochloric acid. In view of this analogy, the ammonium salts are regarded as of the

formula $(NH_3...H)X$, in which one of the hydrogen atoms is differentiated from the others. The same analogy renders it probable that acids should be capable of combining with more than one molecule of ammonia or an amine, and in fact many instances of this are known both as regards ammonia itself, the acid amides, and other derivatives, a large number of examples being adduced. According to this view, the chemical activity of the hydroxyl group of a quaternary ammonium hydroxide is conditioned solely by the special group with which it is associated, whereas in the corresponding carbon compounds of the type $R_3C{\cdot}OH$, the chemical activity of the hydroxyl is influenced by each of the other three groups combined with the same carbon atom (Baeyer and Villiger).

Formamide yields a hydrochloride which, however, has a complex composition. It also yields a *platinichloride*, $(HCO{\cdot}NH_2)_4,H_2PtCl_6$, which crystallises in yellow needles. *Formamide hydrobromide* is a crystalline mass which probably has the composition $(HCO{\cdot}NH_2)_3,2HBr$. *Acetamide hydrobromide*, $(NH_2Ac)_2,HBr$, forms colourless needles, whilst the *hydriodide*, $(NH_2Ac)_2,HI$, crystallises in small, pale yellow needles. *Propionamide hydrobromide* has the normal composition $CH_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2,HBr$, and forms small needles.

Phthalimidine hydrochloride, C_8H_7ON,HCl, is precipitated by hydrogen chloride. The *hydrobromide*, C_8H_7ON,HBr, is a colourless substance and unites with bromine to form a perbromide. *Phthalimidine hydroperbromide*, $(C_8H_7ON)_2,HBr,Br_2$, is formed at once when an aqueous solution of phthalimidine hydrobromide is treated with bromine, and is identical with the substance prepared by Graebe by the action of bromine on phthalimidine dissolved in chloroform, and regarded by him as a simple additive compound $(C_8H_4ON)_2Br_3$ (Abstr., 1889, 140). The *hydroperiodide* cannot be obtained by the action of iodine alone, but is formed when hydriodic acid is also present, and crystallises in lustrous plates possessing a green lustre.

Methylphthalimidine hydroperbromide, $(C_8H_6ONMe)_2,HBr,Br_2$, is prepared in a similar manner and is identical with the bromination product obtained by Graebe and Pictet (Abstr., 1889, 141). The corresponding *hydroperiodide* forms black-green crystals.

The constitution of betaine (Willstätter, *Ber.*, 1902, **35**, 2758) according to this theory would be $\begin{array}{l} CO\text{———————}O \\ | \\ CH_2{\cdot}NMe_2...Me) \end{array}\!\!>$, in which the methyl group is united indirectly with the oxygen atom by a principal valency of its carbon atom, and directly with the nitrogen atom by a supplementary valency. A. H.

The Beckmann Rearrangement. II. JULIUS STIEGLITZ (*Amer. Chem. J.*, 1903, **29**, 49—68. Compare Abstr., 1897, i, 43).—It has been shown previously that if the hydrogen atom of the group $-CO{\cdot}NHBr$ in the acid bromoamides is replaced by an alkyl group, the tendency to undergo the Beckmann rearrangement is suppressed. Similarly, acetylamylchloroamine (Stieglitz and Slosson, Abstr., 1901, i, 462) and the chloroimino-ethers, $R{\cdot}C(NCl){\cdot}OR'$, do not suffer the molecular transformation.

With H. H. Higbee.]—Oxime derivatives in which the possibility of splitting off water from a trivalent nitrogen atom is excluded, refuse to undergo the rearrangement when treated with dehydrating agents; thus, under such conditions, β-benzoyl-β-phenylhydroxylamine yields no trace of diphenylamine.

[With Bernhard C. Hesse.]—It was thought possible that the transformation of acetylbromoamide, for example, may take place in the following manner: $CH_3{\cdot}CO{\cdot}NHBr + 2KOH \rightarrow CH_3{\cdot}CO{\cdot}NH + KBr + KOH \rightarrow OK{\cdot}CO{\cdot}NH{\cdot}CH_3 + KBr$. If this were the case, the rearrangement of trimethylacetylbromoamide would result in the formation of a four-membered ring and the ultimate production of *iso*butylamine; the final product was found, however, to be *ter.*-butylamine, and the possibility of intermediate unstable cyclic compounds is thus excluded.

The interpretations of the Beckmann rearrangement offered by Hoogewerff and van Dorp, Hantzsch, Beckmann, Freundler, and Nef are discussed in turn and shown not to be in agreement with all the facts established in connection with the reaction, whilst all the most important results of the investigation of the reaction from the point of view of the constitution of the substances involved agree best with the explanation previously suggested by the author. E. G.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. VIII. Dithiocarbamic Esters Derived from Ammonia.

Marcel Delépine (*Bull. Soc. chim.*, 1903, [iii], 29, 48—53. Compare Abstr., 1902, i, 271, 595, 597, 702, and Braun, this vol., 13).—The author has prepared a series of dithiocarbamic esters of the type $NH_2{\cdot}CS_2R$ by the action of alkyl haloids on ammonium dithiocarbamate. The esters crystallise well, are readily soluble in organic solvents, and slightly so in water. By alkali hydroxides in alcohol, they are converted into the corresponding mercaptans and alkali thiocyanates, and by acid chlorides or anhydrides into monoacyl derivatives identical with those [acyldithiourethanes] obtained by Wheeler and Merriam by the condensation of thioacetic acid with thiocyanoacetic esters (Abstr., 1901, i, 514). The addition of iodine to solutions of these acyl derivatives in solutions of the alkali hydroxides leads to the precipitation of disulphides, thus with methyl acetyldithiocarbamate, $NHAc{\cdot}CS{\cdot}SMe$, the disulphide, $S_2[C(SMe){:}NAc]_2$, is precipitated, this substance being reconverted by hydriodic acid into the acetyldithiocarbamate. This reaction, together with the solubility in solutions of the alkali hydroxides and non-reactivity with nitrous acid, leads to the representation of the acyl dithiourethanes by the formula $R'CO{\cdot}N{:}C(SR){\cdot}SH$ in place of that given previously.

p-*Nitrobenzyl dithiocarbamate*, $NH_2{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, is the only new ester described; it crystallises in small prisms and melts at 135°.

When ammonium dithiocarbamate is mixed with ethyl chloroacetate, a *substance* is formed having the formula $NH_2{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2Et$, which crystallises in prisms, and when warmed in water or alcohol passes into

the rhodanic acid, $S<\begin{matrix}CS-NH\\ CH_2:CO\end{matrix}$, previously obtained, without the intervention of the intermediate substance, by Miolati (Abstr., 1891, 943).

T. A. H.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. IX. Iminodithiocarbonic Esters. Marcel Delépine (*Bull. Soc. chim.*, 1903, [iii], 29, 53—58. Compare Abstr., 1902, i, 597, and 702).—When dithiocarbamic esters of the type $NH_2{\cdot}CS{\cdot}SR$ (compare preceding abstract) are treated with alkyl iodides in appropriate solvents, the hydriodides of the corresponding iminodithiocarbonic esters, $NH{:}C(SR'){\cdot}SR,HI$, are precipitated. These salts are crystalline, have indefinite melting points, and are soluble in water, but less so in organic solvents; the hydrogen iodide may be directly titrated in presence of phenolphthalein.

Methyl iminodithiocarbonate hydriodide, $NH{:}C(SMe)_2,HI$, forms colourless prisms, melts at about 130°, and decomposes at 140°. *Ethyl iminodithiocarbonate hydriodide* is crystalline, melts between 80° and 90°, and decomposes between 130° and 140°; *benzyl methyl dithiocarbonate hydriodide*, $SMe{\cdot}C(NH){\cdot}S{\cdot}C_7H_7,HI$, forms small, colourless, oblong plates and decomposes at 140°.

From the foregoing salts, acetic anhydride liberates 1 mol. of methyl, ethyl, or benzyl iodide respectively, with the formation of acetyl dithiourethanes. Water, at 100°, converts the hydriodides into the corresponding dialkyl dithiocarbonates and ammonium iodide.

The free esters are obtained by the interaction of ammonia or alkali hydroxides with the salts; they are colourless oils, which decompose, especially when warmed, into the corresponding alkyl thiocyanates or their polymerides and mercaptans. When left in contact with alkali hydroxides, they are converted into alkyl disulphides. Dissolved in dilute hydrochloric acid and treated with sodium nitrite, the esters produce blue solutions, from which ether extracts unstable, crystalline, blue nitroso-derivatives.

The picrates of the esters, on addition of ammonia or alkali hydroxides, give an intense red colour due to the formation of an *iso*purpurate.

T. A. H.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. Marcel Delépine (*Bull. Soc. chim.*, 1903, [iii], 29, 59—60).—*N*-Substituted iminodithiocarbonic esters, $NR{:}C(SR'){\cdot}SR''$, when warmed with dilute hydrochloric acid, are converted into the corresponding dithiocarbonic esters and alkylamines thus: methyl ethyliminodithiocarbonate, $EtN{:}C(SMe)_2$, furnishes methyl thiocarbonate and ethylamine (compare Abstr., 1897, i, 456). *Methyl* N-*acetylmethyldithiocarbamate*, $NMeAc{\cdot}CS{\cdot}SMe$, prepared by acetylating methyl *N*-methyldithiocarbamate (Abstr., 1902, i, 702), is a yellow liquid which distils between 156° and 158° under 32 mm. pressure. *Benzyl* N-*acetylmethyldithiocarbamate*, $NMeAc{\cdot}CS{\cdot}S{\cdot}C_7H_7$, prepared in a similar manner, crystallises in yellow needles and melts at 80°.

T. A. H.

Action of Carbon Monoxide on Potassium Ferricyanide in Solution. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1903, [iii], 29, 24—27).—When an aqueous solution of potassium ferricyanide is heated at 130° with carbon monoxide in sealed tubes, the reactions represented by the following equations take place simultaneously: (*a*) $6K_3Fe(CN)_6 + 7CO + 15H_2O = 6K_3FeCO(CN)_5 + 4NH_4HCO_2 + 2NH_4HCO_3 + CO_2$; (*b*) $7K_3Fe(CN)_6 + 3CO + 15H_2O = 5K_4Fe(CN)_6 + KFeFe(CN)_6 + 6NH_4HCO_2 + 3CO_2$. Quantitative experiments show that the first is the principal reaction, potassium carbonyl ferrocyanide being produced to the extent of 81—94 per cent. of the ferricyanide employed.

The *substance* of the composition $KFeFe(CN)_6$, which is that of potassium ferrocyanide in which three atoms of potassium have been replaced by one atom of "ferric" iron, is produced in minute quantities; it is a greenish powder which dissolves in hydrochloric acid; on addition of water to this solution, Prussian blue is precipitated.

In the absence of water, carbon monoxide has no action on either potassium ferrocyanide or ferricyanide. T. A. H.

Action of Carbon Monoxide on Potassium Mangano-, Cobalti-, Chromi-, and Platino-cyanides. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1903, [iii], 29, 27—31. Compare preceding abstract).—When aqueous solutions of these salts are heated with carbon monoxide at 130° in sealed tubes, there is a slight absorption of the gas in the case of potassium manganocyanide, due possibly to the formation of potassium carbonylmanganocyanide, but more probably to the alkalinity of the reacting liquid, whilst no absorption occurs with the remaining salts.

Potassium platinocyanide and potassium cobalticyanide are practically unchanged by this treatment: the less stable manganocyanide is converted into potassium manganese manganocyanide,

$$K_2MnMn(CN)_6,$$

whilst the chromicyanide is entirely decomposed with the production of chromium sesquioxide, formic and hydrocyanic acids, and ammonia. The reactions of these double cyanides with various metallic salts are tabulated in the original. T. A. H.

Platophosphineammine Compounds. PETER KLASON and J. WANSELIN (*J. pr. Chem.*, 1903, [ii], 67, 41—44. Compare this vol., i, 229).—The action of triethylphosphine on potassium platinichloride leads to the formation of two isomerides (Cahours and Gal), of which the white, stable compound is β-platotriethylphosphine chloride, $Pt(PEt_3Cl)_2$, and the yellow, unstable product is α-platotriethylphosphine chloride, $PEt_3{:}Pt(PEt_3Cl)Cl$. The β-isomeride dissolves easily in aqueous ammonia; with dry ammonia, it forms *platoammine-triethylphosphine chloride*, $Pt(NH_3)_2(PEt_3Cl)_2$, which easily loses ammonia. With phenyl mercaptan in ammoniacal solution, the β-compound yields *platotriethylphosphine phenylmercaptide*,

$$Pt(PEt_3{\cdot}SPh)_2,$$

which crystallises in small, yellowish needles.

Platotriethylphosphineammine chloride, $Pt(PEt_3)_2(NH_3Cl)_2$, formed

when triethyl phosphine and platoämmine chloride are shaken together in chloroform solution, is a white precipitate; it yields a red, crystalline precipitate with potassium platinichloride, and platotriethylphosphine phenylmercaptide when treated with phenyl mercaptan.

G. Y.

Cyclic Compounds. Some Derivatives of *cyclo*Heptane, Suberane, Disuberyl, and Ethylsuberane. Wladimir B. Markownikoff (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 904—916).—A new method is given for the preparation of suberol from suberone, the reduction of which is effected by means of sodium in ethereal alcoholic solution in presence of potassium hydroxide solution. New methods are also given for obtaining suberyl bromide and suberane.

Disuberyl ter.-*glycol*,

$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix},$$

formed during the reduction of suberone, gives aggregates of flat needles melting at 75—76°, whilst if the melted mass is allowed to solidify its melting point then rises to 79—80°; the crystals become strongly electrified when crushed. The pinacone has the normal molecular weight determined cryoscopically in benzene.

On treating suberyl bromide with alcoholic potassium hydroxide, two products are obtained: (1) an *ether* of the composition $C_7H_{11}\cdot OEt$, which is a pleasant-smelling liquid boiling at 173—175°, and (2) *suberene* (suberoterpene), $\begin{matrix}CH_2\cdot CH_2—C\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\geqslant C$, which is a viscous liquid boiling at 120—121° and readily oxidising in the air.

[With L. Jacob.]—*Disuberyl*,

$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}>CH\cdot CH<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix},$$

obtained by the action of sodium on suberyl bromide in ethereal solution, is a colourless, viscous liquid boiling at 290—291° under 728 mm. pressure; it has a sp. gr. 0 9195 at 0°/0° and 0·9069 at 20°/0°; with bromine in presence of aluminium bromide, it yields, among other products, pentabromotoluene.

Ethylsuberane (ethyl*cyclo*heptane), $C_7H_{13}Et$, obtained by the interaction of zinc ethyl and suberyl bromide, is a faintly-smelling, mobile, colourless liquid, which boils at 163—163·5° under 740 mm. pressure and has the sp. gr. 0·8299 at 0°/0°, and 0·8152 at 20°/0°. Oxidation with concentrated nitric acid yields mainly pimelic acid. T. H. P.

Does Suberane occur in Naphtha? Wladimir B. Markownikoff (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 917—918).—By treating various fractions of Caucasian naphtha with concentrated nitric acid, certain mixtures of hydrocarbons are obtained, the analyses and sp. gr. of which indicate that they contain suberane (*cyclo*heptane).

T. H. P.

Auto-oxidation of some Coal-tar Hydrocarbons. Max Weger (*Ber.*, 1903, 36, 309—313).—The reaction given by hydrocarbons with

sulphuric acid is used in the coal-tar industry as a criterion of purity, the pure hydrocarbon showing no coloration at the ordinary temperature. As it has been found that hydrocarbons originally pure show this reaction after being kept, the changes which cause this effect have been investigated. Hydrindene, coal-tar cumene (a mixture of the three trimethylbenzenes), and tetrahydronaphthalene were used in the experiments. Specimens of the hydrocarbons were kept for 15 months exposed to the air and to light; others were exposed to the air, but in darkness; other specimens were sealed up and kept, some exposed to light, and some in darkness, for the same period. It was found that all specimens to which the air had access gave a strong reaction with sulphuric acid, but exposure to light had greatly assisted the change; analysis of the specimens showed that from 7 to 9·4 per cent. of oxygen was absorbed under the influence of light, but only from 0·2 to 0·9 per cent. when kept in darkness; all specimens were acid, but the amount of acid found by titration in the presence of phenolphthalein was not sufficient to account for the oxygen present; there was little difference between the different hydrocarbons, but tetrahydronaphthalene had somewhat the larger quantity of oxygen. Those specimens which were sealed up, whether exposed to light or in darkness, were practically unchanged. K. J. P. O.

Cinnamylidene Chloride. Ernest Charon and Edgar Dugoujon (*Compt. rend.*, 1903, **136**, 94—96).—In order to demonstrate the effect of an adjacent double linking on the characters of an alkyl chloride (compare Charon, Abstr., 1899, i, 469), *cinnamylidene chloride*, $CHPh{:}CH{\cdot}CHCl_2$, which Cahours (*Annalen*, 1847, **70**, 42) failed to obtain by the action of phosphoric chloride on cinnamaldehyde, has been prepared by adding cinnamaldehyde drop by drop to phosphoric chloride, and either distilling the product under reduced pressure, when the chloride passes over last mixed with a little cinnamaldehyde, or by extracting the product with ether, treating the solution successively with sodium carbonate and calcium chloride, and then evaporating the solvent; from the oily residue, crystals begin to separate, which are then placed on porous plates. The compound forms white, nacreous scales melting at 54° and boiling at 142—143° under 30 mm. pressure, reacts with water with the energy of an acid chloride, yielding cinnamaldehyde, and decomposes rapidly in the air, forming cinnamaldehyde, which is then oxidised to cinnamic acid. That the instability is due to the presence of the double linking is shown by the fact that the additive chlorine and bromine products are quite stable. *Tetrachlorophenylpropane*,

$$CHClPh{\cdot}CHCl{\cdot}CHCl_2,$$

crystallises in prisms melting at 66°; *dichlorodibromophenylpropane*, $CHBrPh{\cdot}CHBr{\cdot}CHCl_2$, crystallises in slender needles melting at 127°. K. J. P. O.

Crystallography of some Organic Compounds. F. M. Jaeger (*Jahrb. Min.*, 1903, i, 1—28).—Detailed crystallographic and optical determinations are given for the following substances:—1 : 3 : 4 : 5-tribromotoluene, tetragonal [$a:c = 1:0·3920$]. 1 : 2 : 4 : 5-Tribromotoluene, monoclinic [$a:b:c = 0·9891:1:0·3555$; $\beta = 58°30'22''$]. 2 : 4 : 6-Tri-

chloro-3-nitrobenzoic acid, monoclinic [$a:b:c=1·8710:1:?$; $\beta=75°8'$], or, when crystallised with 1 mol. chloroform, monoclinic [$a:b:c=0·6540:1:0·3333$; $\beta=76°5'30''$]. 2:4:6-Trichloro-3-nitrobenzamide, monoclinic [$a:b:c=1·5933:1:1·0023$; $\beta=65°2'10''$]. The corresponding methylamide, monoclinic [$a:b:c=1·1295:1:0·7112$; $\beta=74°15'46''$]; the methylnitroamide, monoclinic [$a:b:c=0·3010:1:0·3937$; $\beta=85°28'44''$]; the dimethylamide, monoclinic [$a:b:c=1·1164:1:1·1171$; $\beta=50°5'25\frac{1}{2}''$]. Methyl *p*-chlorobenzoate, monoclinic [$a:b:c=1·8626:1:3·4260$; $\beta=64°17'54''$]. Methyl *p*-bromobenzoate, rhombic [$a:b:c=1·3967:1:0·4201$]. Ethyl *p*-methoxycinnamate, monoclinic [$a:b:c=1·3749:1:1·0877$; $\beta=86°26'$]. L. J. S.

Methylethenylbenzene Dibromide. [**$\alpha\beta$-Dibromo*iso*propylbenzene.**] Marc Tiffeneau (*Compt. rend.*, 1902, 135, 1346—1348).—$\alpha\beta$-Dibromo*iso*propylbenzene, $CMePhBr·CH_2Br$, when treated with alcoholic potassium hydroxide, loses a molecule of hydrogen bromide and gives the compound C_9H_9Br. When oxidised with potassium permanganate, this monobromo-compound gives acetophenone, but no bromoacetophenone, and behaves towards magnesium and sodium as does β-bromostyrene; it must therefore be *β-bromo-α-methylstyrene*, CMePh:CHBr. It is a liquid which boils at 105—106° under 9 mm. and at 225—228° under atmospheric pressure, and has a sp. gr. 1·366 at 0°. When fused with potassium hydroxide at 180°, it loses a molecule of hydrogen bromide and is transformed into phenylallylene, CPh:CMe, which boils at 181—185°.

By the action of magnesium on β-bromostyrene, three products are obtained: (1) a magnesium compound, CHPh:CH·MgBr; (2) $\alpha\delta$-diphenylbutadiene (m. p. 149°), obtained by withdrawing 2 atoms of bromine from 2 mols. of β-bromostyrene; and (3) a mixture of phenylacetylene and styrene ($2CHPh:CHBr + Mg = CPh:CH + CHPh:CH_2 + MgBr_2$) due to elimination of hydrogen bromide. The phenylacetylene acts on the magnesium compound to form styrene and a second magnesium compound, CPh:C·MgBr. By the action of water on the reaction mixture, phenylacetylene and styrene are formed, but if the magnesium compounds are first decomposed with carbon dioxide, phenylpropiolic and cinnamic acids are obtained.

Sodium removes hydrogen bromide from β-bromostyrene and sodium phenylacetylene is formed. Sodium and magnesium react in a similar manner on the bromides $CHPhBr·CH_2Br$ and $CPhBr:CH_2$.

By the action of magnesium on β-bromo-α-methylstyrene, there are formed: (1) a magnesium compound, CMePh:CH·MgBr, (2) $\beta\epsilon$-diphenyl-$\Delta^{2\cdot4}$-hexadiene of melting point 138°, and (3) a mixture of the hydrocarbons C_9H_8 and C_9H_{10}. The hydrocarbon C_9H_8 is not a true acetylenic hydrocarbon, because it does not react with the magnesium compound first produced to give a magnesium acetylide. The only substance formed on which carbon dioxide can react is CMePh:CH·MgBr, and from it two non-acetylenic acids are formed which melt at 80° and 130° respectively: these are probably the two stereoisomeric β-methylcinnamic acids. J. McC.

Aromatic Propylene Derivatives. CARL HELL and HERMANN BAUER (*Ber.*, 1903, 36, 204—208. Compare Hell and Portmann, Abstr., 1896, i, 357 ; Hell and Hollenberg, *ibid.*, 354).—Allylbenzene, prepared by Grignard's method (Abstr., 1900, i, 382), yields a dibromide melting at 66°. An alcoholic solution of sodium ethoxide reacts with the dibromide yielding *β-bromoallylbenzene*, which distils at 109—110° under 20 mm. pressure, has a sp. gr. 1·35 at 20°, and a characteristic odour. Prolonged treatment with excess of sodium ethoxide does not decompose it. J. J. S.

Experiments on the Reduction of Nitrobenzene. WILHELM H. GINTL (*Zeit. angew. Chem.*, 1902, 15, 1329—1336).—It has been observed by Storch that benzidine is formed when nitrobenzene is reduced by zinc dust in the presence of hydrochloric acid. A systematic investigation of the conditions under which benzidine is produced has shown that metals reduce nitrobenzene in acid solution primarily to phenylhydroxylamine, which then may change in two directions, one generally predominating according to the conditions. Either the phenylhydroxylamine gives azobenzene, which is then reduced to hydrazobenzene, the latter being transformed into benzidine, or the hydroxylamine is reduced directly to aniline. K. J. P. O.

Nitration of Benzyl Chloride. FREDERICK J. ALWAY (*J. Amer. Chem. Soc.*, 1902, 24, 1060—1063).—To determine the conditions under which the maximum yield of *p*-nitrobenzyl chloride is obtained, various methods of nitration were tried, with the result that even under the most favourable conditions, namely, with fuming nitric acid, much concentrated sulphuric acid, and a temperature below $-5°$, the yield was only 50 per cent. of that calculated. The oily by-product formed is shown to consist of nitrobenzyl chlorides, in some cases mixed with dinitrobenzyl chloride. E. F. A.

Disulphones. XII. Mixed Disulphones. THEODOR POSNER [with ROBERT HAZARD] (*Ber.*, 1903, 36, 296—304. Compare Abstr., 1899, i, 604 ; 1900, i, 5, 16 ; 1901, i, 14, 88, 474, 703 ; 1902, i, 82, 220, 296, 622).—Aldehydes and α-keto-acids combine directly with mercaptans to yield additive compounds of the type $R·CH(OH)·SEt$, which then react with a further quantity of mercaptan under the influence of condensing reagents (such as dry hydrogen chloride), yielding mercaptals of the type $R·CH(SEt)_2$, which can then be oxidised to disulphones. When a different mercaptan is employed in the second reaction, mixed mercaptals of the type $R·CH(SEt)·SMe$ are obtained, although in many cases the yields are not good owing to the production of the simple mercaptals.

Ketones do not form additive compounds with mercaptans, but in the presence of condensing agents react with the mercaptans yielding mercaptals. Even when a mixture of two mercaptans is employed, the product consists of the two simple mercaptals.

Diamylsulphonemethane (formaldehydediamylsulphone),

$$CH_2(SO_2·C_5H_{11})_2,$$

forms feathery needles melting at 138—139° and readily soluble in alcohol.

as-*Diamylsulphone-ethane* (*acetaldehydediamylsulphone*),

$$CHMe(SO_2 \cdot C_5H_{11})_2,$$

is insoluble in water and melts at 130°. as-*Dibenzylsulphone ethane* (*acetaldehydedibenzylsulphone*) melts at the same temperature. *Diamylsulphonephenylmethane* (benzaldehydediamylsulphone),

$$CHPh(SO_2 \cdot C_5H_{11})_2,$$

crystallises in colourless needles melting at 99—100°. The corresponding mercaptal may be obtained without the aid of a condensing agent.

a-Benzylthiolhydroxypropionic acid, $OH \cdot CMe(S \cdot C_7H_7) \cdot CO_2H$, obtained by the addition of benzyl mercaptan to pyruvic acid, has only been obtained in an amorphous state melting at 82°. On condensation with a second molecule of benzyl mercaptan, it yields *aa-dibenzylthiolpropionic acid*, $CO_2H \cdot CMe(S \cdot C_7H_7)_2$, melting at 98—100° and readily soluble in all organic solvents.

Good yields of *phenylethyldisulphonemethane* (*formaldehydephenylethyldisulphone*), $SO_2Et \cdot CH_2 \cdot SO_2Ph$, melting at 110—111°; *phenylbenzyldisulphonemethane*, melting at 145—147°, and *phenylethyldisulphonephenylmethane*, $SO_2Et \cdot CHPh \cdot SO_2Ph$, melting at 155—156°, may be obtained by the method described.

The amounts of the following compounds produced are usually small owing to the formation of the simple sulphones, from which the mixed compound can only be separated by repeated fractional crystallisation. *Benzylethyldisulphonemethane*, $SO_2Et \cdot CH_2 \cdot SO_2 \cdot C_7H_7$, melting at 172—174°; *phenylamyldisulphonemethane*, melting at 86—88°; *phenylbenzyldisulphone-ethane*, $SO_2Ph \cdot CHMe \cdot SO_2 \cdot C_7H_7$, melting at 144°; *benzylamyldisulphonephenylmethane*, $SO_2C_5H_{11} \cdot CHPh \cdot SO_2 \cdot C_7H_7$, melting at 145°; and *phenylbenzyldisulphonephenylmethane*, melting at 173—174°.

The following mixed derivatives of pyruvic acid have been prepared: *a-phenylthiol-a-ethylthiolpropionic acid* (*pyruvic acid phenylethylmercaptal*), $SEt \cdot CMe(SPh) \cdot CO_2H$, colourless crystals from benzene, melting at 98—99°; *a-phenylthiol-a-amylthiolpropionic acid* (*pyruvic acid phenylamylmercaptal*), in the form of an oil, and *a-phenylthiol-a-benzylthiolpropionic acid* melting at 72°. When oxidised in chloroform solution with permanganate, the mixed mercaptals give the corresponding mixed sulphones of acetaldehyde in consequence of the elimination of carbon dioxide.

Phenylethyldisulphone-ethane (*acetaldehydephenylethyldisulphone*) melts at 97—99°, and the corresponding *phenylamyl* compound at 84—86°.

Mixed disulphones of acetone may be obtained indirectly by the methylation of mixed sulphones derived from acetaldehyde by the aid of methyl iodide and sodium hydroxide: $SO_2X \cdot CHMe \cdot SO_2Y \rightarrow SO_2X \cdot CMe_2 \cdot SO_2Y$.

Phenylethyldisulphonedimethylmethane (*acetonephenylethyldisulphone*), $SO_2Et \cdot CMe_2 \cdot SO_2Ph$, melts at 78—80°, and the corresponding *phenylbenzyl* compound at 125—126°. J. J. S.

Formula of Triphenylmethyl with Quadrivalent Carbon. E. Heintschel (*Ber.*, 1903, **36**, 320—322).—Gomberg's determinations of the mol. weight of triphenylmethyl, which he represents by a

formula in which one of the carbon atoms is tervalent, do not agree well with the unimolecular formula $C_{19}H_{15}$; the latter requires a mol. weight 243, whereas the values 330 and 372 were found (Abstr., 1901, i, 77). It is maintained that triphenylmethyl would be better represented by a dimolecular formula, in which two of the benzene nuclei have a quinonoid structure, thus:

$$CPh_2{:}C{<}{\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}}{>}CH{\cdot}CH{<}{\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}}{>}C{:}CPh_2.$$

This formula would not only account for the slight stability of the substance, but also for its conversion by chlorine, bromine, &c., into triphenylmethyl chloride, &c., and its ready oxidation; further, the intensely yellow colour of the solutions of triphenylmethyl would then be correlated with the same structural peculiarity which Thiele (Abstr., 1900, i, 298) supposes to exist in his coloured hydrocarbon, fulvene. K. J. P. O.

Triphenylmethyl. VII. Condensation by Hydrochloric Acid to Hexaphenylethane. Moses Gomberg (*Ber.*, 1903, **36**, 376—388).—The condensation of triphenylmethyl to hexaphenylethane is not brought about by the pure chloro-ethers $Cl{\cdot}CH_2{\cdot}OR$, but by the hydrogen chloride which is so readily produced from them; condensation can readily be effected by dissolving the triphenylmethyl in benzene containing either much or little hydrogen chloride, or by adding an ethereal solution of hydrogen chloride to a solution of the hydrocarbon in benzene.

The formation of hexaphenylethane in place of triphenylmethyl by the action of silver or tin on a hot solution in acetic acid of triphenylchloromethane is also due to the production of hydrogen chloride by a reversible action, $CPh_3Cl + HOAc \rightleftarrows CPh_3{\cdot}OAc + HCl$; zinc behaves somewhat differently, considerable quantities of triphenylmethane being produced and only small amounts of hexaphenylethane. In all cases, the first product is probably triphenylmethyl.

Triphenylmethyl can be prepared very satisfactorily by reducing a solution of the chloride in acetic acid by means of zinc dust at the atmospheric temperature, cautiously precipitating the hydrocarbon with water, and recrystallising from benzene.

The production of hexaphenylethane from triphenylcarbinol (Ullmann and Borsum, Abstr., 1902, i, 755) is probably not a direct condensation, and it is suggested that the chloride is formed by a reversible action, $CPh_3{\cdot}OH + HCl \rightleftarrows CPh_3Cl + H_2O$, and is reduced to triphenylmethyl, which then undergoes condensation.

By acting on triphenylchloromethane with mercury, it is shown that chlorine is removed and not hydrogen chloride, since the latter would bring about polymerisation of the triphenylmethyl produced.

T. M. L.

Preparation of Adjacent (*aaa*) Triphenylethane. M. Kuntze-Fechner (*Ber.*, 1903, **36**, 472—475).—*Triphenylethane*, $CPh_3{\cdot}CH_3$, is prepared by heating triphenylbromomethane with zinc methide in benzene solution, and crystallises in colourless, monoclinic (?) needles melting at 95°. The hydrocarbon closely resembles triphenylmethane in appearance and melting point, as well as in the reactions of its

nitro-derivative. The nitro-derivative of triphenylmethane, however, develops a violet coloration with alcoholic potassium hydroxide which is not given by the triphenylethane derivative. All attempts to oxidise or brominate the hydrocarbon proved unsuccessful. On nitration, it yields a *trinitro*-derivative, which crystallises in short, thick needles and melts at 200—202°. The corresponding *triamino*-compound crystallises in large, light pink plates melting at 191—192°. When gently heated on platinum foil, it gives a magenta coloration.

It was found impossible to prepare the hydrocarbon either by the action of benzene on methylchloroform in presence of aluminium chloride, or by the distillation of calcium formate with calcium triphenylacetate. No homologue of the hydrocarbon could be prepared by acting on triphenylbromomethane with zinc ethyl, ethylene being formed together with triphenylmethane. A. H.

Preparation of Tetraphenylmethane. Fritz Ullmann and A. Münzhuber (*Ber.*, 1903, **36**, 404—410).—Triphenylcarbinol is best prepared by adding an ethereal solution of methyl benzoate to the product obtained by the interaction of magnesium and bromobenzene in anhydrous ether; the yield is 87 per cent., that of theory. When the carbinol is boiled for 5—6 hours with aniline hydrochloride in glacial acetic acid solution, and the product, after diluting with water, heated with sodium acetate, *aminotetraphenylmethane*, $CPh_3\cdot C_6H_4\cdot NH_2$, is obtained; this crystallises from toluene in nearly colourless leaflets, melts at 256° (corr.), and gives a *hydrochloride* which crystallises in leaflets and melts at 271°. On diazotising the hydrochloride of the base in glacial acetic acid by means of amyl nitrite and combining the salt with dimethylaniline, *tetraphenylmethaneazodimethylaniline*, $CPh_3\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$, is obtained, which crystallises from glacial acetic acid in red needles and melts at 258° (corr.). If the solid diazonium sulphate is boiled with alcohol, it gives tetraphenylmethane, which crystallises from glacial acetic acid in long, slightly yellow needles, melts at 282° (Gomberg, Abstr., 1897, i, 623, gives 267·5°), and boils at 431° under 760 mm. pressure. W. A. D.

Synthesis of an Aromatic Hydrocarbon derived from Camphor. Camille Chabrié (*Compt. rend.*, 1902, **135**, 1348—1350). —To a mixture of chlorocamphor and benzene heated in a reflux apparatus, aluminium chloride was added in small quantities at a time. After heating for about four hours, the colour of the benzene suddenly changed to red. The amount of hydrogen chloride evolved was greater than corresponds with 1 molecule from 1 molecule of chlorocamphor, and this is attributed to an elimination of water which gives hydrogen chloride with the aluminium chloride. After treatment with water, &c., the following products were obtained; a liquid boiling at from 160—250° which rapidly becomes violet in colour; a clear, yellow liquid boiling at 250—305°; an almost colourless, mobile liquid boiling at 305—325°; a reddish liquid boiling at 325—342°; a reddish liquid boiling at 342—362°, which deposited a small quantity of yellow crystals; and a substance boiling above 360°, which solidifies

on cooling to yellow crystals melting above 100°, and soluble in alcohol. By redistilling the fraction boiling at 305—325°, an almost colourless hydrocarbon was isolated having the formula $C_{16}H_{18}$; it boils at 315°, and is formed according to the equation $C_{10}H_{15}ClO + C_6H_6 = C_{10}H_{13}Ph + H_2O + HCl$. J. McC.

Determination of the Specific Heat and Latent Heat of Evaporation of Aniline. W. A. Kurbatoff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 766—787).—The author has obtained the following mean results for the specific heat of aniline over certain ranges of temperature: between 18° and 78°, 0·5025; 20° and 138°, 0·5231; 20° and 158°, 0·5191; 20° and 172°, 0·5254; 20° and 184°, 0·5301; 20° and 180°, 0·5288. These results show that up to about 137° the specific heat of aniline increases; then it begins to fall at about 158°, reaches a minimum, and afterwards again increases.

For the latent heat of evaporation at 184·3° and under 756 mm. pressure, the mean value 109·6 has been obtained.

Trouton's formula gives a number 22·3, showing that aniline is but slightly associated at its boiling point.

Using Ramsay's numbers for the boiling points of aniline under different pressures, the coefficient dp/dt is found to have the value 0·02565 at the boiling point.

The density of the saturated vapour calculated by the Clausius-Clapeyron formula at the boiling point has the almost theoretical value 48·3. This number diminishes as the pressure decreases, reaches a minimum, and afterwards rises.

The changes just mentioned in the specific heat of aniline are probably connected with the changes in its degree of association indicated by the latent heat and vapour density determinations.

T. H. P.

Condensation of Chloral with the Nitroanilines. Alvin S. Wheeler and H. R. Weller (*J. Amer. Chem. Soc.*, 1902, **24**, 1063—1066).—The compounds described were prepared by mixing their components in benzene solution. Trichloroethylidene di-*o*-nitroaniline, $CCl_3{\cdot}CH(NH{\cdot}C_6H_4{\cdot}NO_2)_2$, crystallises from hot alcohol in yellow, rectangular plates melting at 171°. The corresponding *meta*-compound melts at 212°, whilst the *para*-derivative forms a yellow powder, insoluble in most solvents, melting at 216° (compare also Eibner, Abstr., 1899, i, 41). E. F. A.

Compounds of Aniline Sulphite with Aldehydes. C. Speroni (*Annalen*, 1902, **325**, 354—361).—Eibner (Abstr., 1901, i, 376) has stated that in most cases aniline sulphite and an aldehyde yield a single compound, $R{\cdot}CH{:}NPh$ or $R{\cdot}CH(NHPh)_2$, although occasionally both are formed. The author's investigations show that generally several compounds are produced when an aldehyde reacts with aniline and sulphurous acid.

The *compound* $C_7H_{14}O,2NH_2Ph,H_2SO_3$ is obtained as a red oil when heptaldehyde is shaken with an aqueous solution of aniline sulphite; on washing with ether, it forms a white, crystalline powder

melting and decomposing at 100°, and when boiled with alcohol is converted into heptylideneaniline. The compound $C_7H_{14}O,2NH_2Ph,SO_2$ is formed when heptaldehyde is added to an ethereal solution of aniline which has been saturated with sulphur dioxide; it is a white powder melting and decomposing at 98°. On adding *iso*valeraldehyde (1 mol.) to an aqueous solution of aniline sulphite (2 mols.), the *compound* $C_5H_{10}O,2NH_2Ph,H_2SO_3$ separates as a white, crystalline powder melting at 115—117°. The *compound* $C_5H_{10}O,2NH_2Ph,SO_2$, prepared in the same manner as the analogous derivative of heptaldehyde, is a white, crystalline powder melting and decomposing at 122—124°. Benzaldehyde yields the *compound* $C_7H_6O,2NH_2Ph,H_2SO_3$, which is a yellowish, crystalline substance melting at 130°, and the *compound* C_7H_6O,NH_2Ph,H_2SO_3, the latter being formed when the sulphur dioxide is in excess; it crystallises in bluish leaflets melting at 135°, and when treated with aniline is converted into the compound first mentioned. The *compound* $C_7H_6O,2NH_2Ph,SO_2$ is formed as a white, crystalline powder when benzaldehyde is added to an ethereal solution of aniline saturated with sulphur dioxide, and melts with evolution of gas at 138—140°. Salicylaldehyde also forms three compounds, the *additive* product, $C_7H_6O_2,2NH_2Ph,H_2SO_3$, which melts at 115°, the *substance*, $C_7H_6O_2,NH_2Ph,H_2SO_3$, a yellowish, crystalline powder melting at 118—121°, and the *compound* $C_7H_6O_2,2NH_2Ph,SO_2$, which is a yellow powder melting and decomposing at 99°. Three series of compounds are thus formed according as a neutral or strongly acid aqueous solution or an ethereal solution is used. K. J. P. O.

Formaldehyde Derivatives of Aromatic Bases. CARL A. BISCHOFF and F. REINFELD (*Ber.*, 1903, 36, 41—53).—The interaction of *m*-toluidine with aqueous formaldehyde gives two isomeric *anhydroformaldehyde*-m-*toluidines*, $(C_6H_4Me\cdot N\colon CH_2)_n$, which are both amorphous and strongly electric and melt respectively at 148—149° and 183—184°; the latter is more soluble in ether than the former, and is converted into it when dissolved in benzene. *Methylenedi*-m-*toluidine*, $CH_2(NH\cdot C_6H_4Me)_2$, obtained by adding aqueous formaldehyde to a warm mixture of *m*-toluidine and alcoholic potassium hydroxide, boils at 146° under 13 mm. pressure, but is thereby partly decomposed, giving *m*-toluidine and the anhydro-compound.

Methylenedi-o-*chloroaniline*, $CH_2(NH\cdot C_6H_4Cl)_2$, prepared from *o*-chloroaniline and aqueous formaldehyde, crystallises from benzene and melts at 84°; *methylenedi*-m-*chloroaniline* crystallises from light petroleum in nodular aggregates of needles and melts at 73°; *methylenedi*-p-*chloroaniline* forms long, six-sided prisms and melts at 65°.

Anhydroformaldehyde-m-*chloroaniline*, $(C_6H_4Cl\cdot N\colon CH_2)_n$, is an amorphous powder melting at 228°, which, on crystallisation from ethylene dibromide, is converted into an *isomeride* (?) melting at 176°. *Anhydroformaldehyde*-p-*chloroaniline* exists in two forms, both having the formula $(C_6H_4Cl\cdot N\colon CH_2)_3$; they melt at 225° and 157°, the latter being the more soluble in ether. On heating the former with benzene, or the latter alone in a vacuum at 150°, conversion into the isomeride occurs.

Methylenedi-o-*anisidine*, $C_{15}H_{18}O_2N_2$, crystallises from a mixture of benzene and light petroleum in rectangular plates and melts at 86°. The analogous *p*-anisidine derivative melts at 66°, and when crystallised from alcohol is converted into the *anhydro-base*,

$$(OMe \cdot C_6H_4 \cdot N \colon CH_2)_n,$$

which separates in microscopic prisms and melts at 132°.

Methylenedi-*p*-phenetidine (Abstr., 1899, i, 278), which melts at 89°, not at 80°, does not undergo change when crystallised from alcohol.

From *m*-aminobenzoic acid and formaldehyde, no definite product could be obtained, but *p*-aminobenzoic acid gave *methylenedi*-p-*aminobenzoic acid*, $C_{15}H_{14}O_4N_2$, which is hygroscopic and melts at 167—168°.

W. A. D.

Derivatives of Diphenylamine and Tolylphenylamine. FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1903, **36**, 29—35).—2′:4′-Dinitrophenyl-*o*-tolylamine, obtained by heating a mixture of *o*-toluidine, dinitrochlorobenzene, and fused sodium acetate for an hour at 200°, crystallises from a mixture of alcohol and acetone in lemon-yellow prisms, and melts at 129°, not at 101—102°, as previously stated. With nitric acid of sp. gr. 1·2, it gives a mixture of a *mononitro*-derivative crystallising in small, reddish-brown prisms, melting at 158°, and a *dinitro*-derivative which forms yellow prisms, and melts at 190°.

2 : 4 : 6-*Trinitrophenyl*-o-*tolylamine*, obtained from *o*-toluidine and picryl chloride, crystallises from a mixture of alcohol and acetone in orange-red prisms, and melts at 164°.

2 : 4-*Dinitrophenyl*-m-*tolylamine* crystallises in small clusters of needles, and melts at 161°. The analogous *p*-tolyl derivative, which is already known, gives, on nitration, a *tetranitrophenyl*-p-*tolylamine*, which crystallises from alcohol in thick, reddish-brown prisms, and melts at 219°.

2-*Chloro*-2′ : 4′-*dinitrodiphenylamine*, obtained from *o*-chloroaniline and 2 : 4-dinitrochlorobenzene, crystallises in long, golden-yellow needles, and melts at 148—149° ; on nitration, it gives 2-*chloro*-4 : 2′ : 4′-*trinitrodiphenylamine*, which crystallises from acetone in small, yellow prisms, melts at 165—166°, and is also obtained by chlorinating 4 : 2′ : 4′-trinitrodiphenylamine.

3-*Chloro*-2′ : 4′-*dinitrodiphenylamine* crystallises from dilute acetone in yellowish-red, felted needles, melts at 182—183°, and on nitration gives a slightly impure *chlorotrinitrodiphenylamine* melting at 209°.

4-*Chloro*-2′ : 4′-*dinitrodiphenylamine* forms slender, orange-red needles, melts at 165°, and on nitration yields a p-*chlorotetranitrodiphenylamine*, crystallising in amber-coloured prisms and melting at 182—183°. 2 : 4-*Dichloro*-2′ : 4′-*dinitrodiphenylamine*, from 2 : 4-dichloroaniline, forms long, yellow needles, melts at 166°, and on nitration gives a *dichlorotetranitrodiphenylamine* melting at 198°.

The following compounds were obtained by condensing 2 : 4-dinitrochlorobenzene with *o*-toluidine-*p*-sulphonic acid, *p*-toluidine-*o*-sulphonic acid, and their amides. *Sodium* 4-*methyl*-2′ : 4′-*dinitrodiphenylamine*-3-*sulphonate* crystallises in long, red prisms, and the analogous derivative from *o*-toluidine-*p*-sulphonic acid in yellow prisms ; the

respective *amides* melt at 255° and 209° and crystallise in yellow prisms. W. A. D.

Benzidine Transformations. J. Potter van Loon (*Proc. K. Akad. Wetensch. Amsterdam.*, 1903, 5, 377—378).—Benzidine can be quantitatively estimated by precipitation with potassium sulphate from a slightly acid solution, and collecting the sulphate on a weighed paper. Benzidine sulphate is soluble in water to the extent of about 5—6 mg. per 100 c.c. at the ordinary temperature.

Weighed quantities of hydrazobenzene were shaken with a known quantity of acid until the whole dissolved, and the benzidine formed was then estimated. At the ordinary temperature, $N/10$ hydrochloric acid converts 84 per cent. of the hydrazobenzene into benzidine, whilst normal hydrochloric or hydrobromic acid converts 90 per cent. in a similar manner. At 100°, $N/10$ hydrochloric acid only transforms 66·4 per cent. of the hydrazobenzene into benzidine.

The velocity of the reaction at 25° appears to depend on the concentration of the acid, but it increases more rapidly than the concentration. J. McC.

Method of forming Phenols. F. Bodroux (*Compt. rend.*, 1903, **136**, 158—159).—Organo-magnesium compounds are decomposed by the air; the moisture present causes a liberation of the hydrocarbon, and the oxygen directly oxidises the substance ($R·MgBr + O = R·O·MgBr$); the oxidised product is decomposed by acid, and phenol is formed ($R·O·MgBr + HCl = R·OH + ClMgBr$). A yield varying from 5 to 10 per cent. of phenol can be obtained by passing a current of dry air, free from carbon dioxide, through an ethereal solution of the organo-magnesium bromide, and then decomposing the residue, left after the evaporation, with acid. In this way, phenol, cresols, and ethers of quinol have been obtained from bromobenzene, *o*- and *p*-bromotoluenes, *p*-bromoanisole, and *p*-bromophenetole respectively. J. McC.

Phenoxyethylene, Phenoxyacetylene, and their Derivatives. Max Slimmer (*Ber.*, 1903, **36**, 289—295. Compare Sabanéeff and Dworkowitsch, *Annalen*, 1882, **216**, 283).—Tribromoethylene, obtained by the action of alcoholic potash on acetylene tetrabromide, reacts with alcoholic potassium phenoxide, yielding Sabanéeff and Dworkowitsch's phenoxydibromoethylene melting at 36—37°.

When the dibromo-compound is heated with alcoholic potash for 7 hours at 110°, it yields ethyl bromoacetate and not phenoxybromoacetylene as stated by Sabanéeff and Dworkowitsch. A small amount of the acetylene compound may be obtained by the action of metallic sodium on the dibromo-derivative. *αββ-Tribromo-α-phenoxyethylene*, $CBr_2{:}CBr·OPh$, obtained by the action of alcoholic potash on phenoxytetrabromoethane, melts at 94°, does not combine with bromine, and on treatment with sodium, yields the sodium derivative of phenoxyacetylene.

β-Bromo-α-phenoxyethylene (compare Sabanéeff) is readily obtained by the action of alcoholic sodium phenoxide on acetylene dibromide. It distils at 115—116° under 15 mm. pressure and has a sp. gr.

1·466 at 14°/4°. Its *dibromide* is a thick oil distilling at 191° under 15 mm. pressure, and on treatment with alcoholic potash yields *αβ-dibromo-α-phenoxyethylene* in the form of an oil distilling at 155·8° under 25 mm. pressure, which has a sp. gr. 1·805 at 21°/4°, and combines with bromine, yielding tetrabromo-α-phenoxyethane, which distils at 200° under 15 mm. pressure.

Phenoxyacetylene, which may readily be obtained by distilling β-bromo-α-phenoxyethylene with powdered potassium hydroxide under reduced pressure, distils at 75° under 35 mm. pressure, has an odour resembling that of phenylacetylene, and yields *sodium*, *silver*, and *copper* derivatives of the type AgC⋮C·OPh. J. J. S.

Phytosterol contained in Olive Oil. GIOVANNI SANI (*Chem. Centr.*, 1903, i, 93; from *Staz. sperim. agrar. ital.*, **35**, 701—705).—The chloroform solution of the cholesterol obtained in experiments on the germination of the olive (Abstr., 1900, ii, 613) was found to give a somewhat abnormal coloration with sulphuric acid. In order to determine the relationship between the phytosterol contained in the olive seedlings and that in the fruit or oil, the higher alcohols were isolated from the oil by Bömer's method (Abstr., 1899, ii, 191, 192). An olive oil from San Valentino, Perugia, having n_D 61·9 at 25°, when thus treated, yielded an oil and a solid compound. The *oil* is soluble in cold absolute alcohol, even more so in hot, very readily so in ether, benzene, or carbon disulphide, and insoluble in water or dilute alcohol. The solid *compound*, $C_{26}H_{44}O,H_2O$, crystallises from a mixture of alcohol with a small quantity of ether in lustrous needles, melts at 134°, and has α_D − 28·9 in chloroform solution (200 mm. tube). Although the percentage composition of this compound corresponds with that of the ordinary cholesterols and phytosterols, when heated with benzoic anhydride at 125—130° it forms a *derivative* which crystallises from ether in lustrous, trimetric crystals which are not identical with those of cholesterol benzoate (compare Fock, *Zeit. Kryst. Min.*, **21**, 243); it is lævorotatory and melts at 149°. E. W. W.

Derivatives of Phenyl Ether. III. ALFRED N. COOK and CHARLES F. EBERLY (*J. Amer. Chem. Soc.*, 1902, **24**, 1200—1204. Compare Abstr., 1901, i, 144; 1902, i, 92).—p-*Nitrophenyl* o-*tolyl ether*, $NO_2·C_6H_4·O·C_6H_4Me$, prepared by heating a molecular mixture of *p*-bromonitrobenzene and potassium *p*-cresoxide in an oil-bath at 135°, is a reddish-brown liquid which is miscible with the common organic solvents and boils at 220—222° under a pressure of 27 mm. When heated on the water-bath with sulphuric acid, it gives a *monosulphonic acid*, which forms needle-like crystals, melts at 115°, and is soluble in acids, alcohol, or hot benzene. The *barium* salt, $(C_{13}H_{10}O_6NS)_2Ba$, is very sparingly soluble; 1000 parts of water dissolving 13·27 parts at 100° and 3·77 parts at 24°. The *copper* salt crystallises with $5H_2O$. The *sodium* salt melts at 233° and the *potassium* salt at 205°.

p-Aminophenyl o-*tolyl ether hydrochloride*, $C_6H_4Me·O·C_6H_4·NH_2,HCl$, obtained by reduction with tin and hydrochloric acid, crystallises in long needles and scales, melts at 182—183°, is soluble in alcohol, but insoluble in benzene and ether. The free *base* is soluble in alcohol or

benzene, but insoluble in ether, and melts at about 60°. The *nitrate* melts at 153—155°, the *sulphate* at 155—160°, the *hydrobromide* at 200—204°, and the *platinichloride* at 180—190°.

When the nitro-ether is treated with nitric acid, a *dinitrophenyl o-tolyl ether* is formed. It melts at 125°, and is soluble in ether, benzene, nitrobenzene, or aniline; it could not be reduced to an amino-compound. J. McC.

Action of Sodium on γ-Phenoxypropyl Iodide. Diphenoxyhexane. Jules Hamonet (*Compt. rend.*, 1903, **136**, 96—98).—Since the boiling points of hexamethylene glycol (b. p. 235—240°; Haworth and Perkin, Trans., 1894, **65**, 591) and of tetramethylene glycol (b. p. 230°; Hamonet, Abstr., 1901, i, 251) lie apparently only 5° apart, a new preparation of the former glycol has been undertaken. It was first attempted to prepare this glycol from γ-amyloxybutyl cyanide, $C_5H_{11}O\cdot[CH_2]_3\cdot CN$, which is a liquid boiling at 108—110° under 12 mm. pressure; γ-amyloxybutyric acid, a liquid boiling at 148° under 15 mm. pressure, was prepared from the substance last mentioned, and in the form of its potassium salt submitted to electrolysis; the compound was hydrolysed, however, amyl alcohol being formed, and a mixture of products resulting from the electrolysis of γ-hydroxybutyric acid. A similar attempt made by Noyes (Abstr., 1898, i, 59) to prepare a hexamethylene derivative by the same method from γ-ethoxybutyric acid gave an unsatisfactory result. The preparation of *diphenoxyhexane*, $OPh\cdot[CH_2]_6\cdot OPh$, was attempted by Funk (Abstr., 1894, i, 34) and Solonina (*ibid.*, 119) by the action of sodium on phenoxypropyl chloride or bromide; in neither case could more than a trace of the hexane derivative be obtained, the main reaction resulting in the production of sodium phenoxide, propylene, and trimethylene. When the corresponding iodide is used, however, diphenoxyhexane can be easily prepared. *γ-Phenoxypropyl iodide*, $OPh\cdot CH_2\cdot CH_2\cdot CH_2I$, is prepared by boiling phenoxypropyl bromide with sodium iodide in alcoholic solution; it is a colourless liquid boiling at 155—156° under 16 mm. pressure, and at low temperatures solidifies to crystals melting at 12°; it has a sp. gr. 1·585 at 18°. When treated with sodium in very dilute ethereal solution at 0°, a very good yield of diphenoxyhexane (m. p. 83°; Solonina, *loc. cit.*) is obtained. Attention is called to the fact that with sodium, phenoxyethyl iodide gives mainly ethylene. K. J. P. O.

Action of Benzenesulphinic Acid on Phenols and Aromatic Amines. Oscar Hinsberg (*Ber.*, 1903, **36**, 107—115).—Benzenesulphinic acid combines not only with quinones, but also with phenols to form sulphides or sulphones and with amines to form sulphides or sulphoxides.

Methoxydiphenyl sulphide, $OMe\cdot C_6H_4\cdot SPh$, prepared by methylating the product of interaction of phenol and benzenesulphinic acid, is a colourless, mobile oil of not unpleasant odour, and boils at 180—185° under 12 mm. pressure. *Hydroxydiphenyl sulphide*, $OH\cdot C_6H_4\cdot SPh$, was obtained in a fairly pure state by hydrolysing the methyl ether; it is a thick liquid, which dissolves only slightly in water, but readily in dilute sodium hydroxide.

Phenylthiol-2-hydroxybenzoic acid, $CH\cdot C_6H_3(SPh)\cdot CO_2H$, prepared from benzenesulphinic and salicylic acids, crystallises from methyl alcohol in small, colourless needles, and melts at 168°.

Phenyl-*p*-dihydroxyphenylsulphone, $PhSO_2\cdot C_6H_3(OH)_2$, is produced when benzenesulphinic acid and quinol are fused together on the water-bath. Phenyl-*o*-dihydroxyphenylsulphone, prepared from catechol and benzenesulphinic acid, is isomeric with the compound which Hinsberg and Himmelschein (Abstr., 1896, i, 685) obtained by oxidising catechol in presence of benzenesulphinic acid, but identical with that which Jackson and Koch obtained by the action of benzenesulphinic acid on the product of oxidation of catechol by iodine (Abstr., 1898, i, 518).

p-*Aminodiphenylsulphoxide*, $NH_2\cdot C_6H_4\cdot SOPh$, prepared from aniline and benzenesulphinic acid, crystallises from water in colourless needles, melts at 152°, and forms a diazo-compound; it is reduced to the sulphide by zinc-dust and hydrochloric acid. *p*-Aminodiphenyl sulphide, $NH_2\cdot C_6H_4\cdot SPh$, prepared from aniline hydrochloride and benzenesulphinic acid, crystallises from dilute methyl alcohol in colourless needles, and melts at 95°; it has basic properties, forms a diazo-compound, and is identical with the compound melting at 93°, described by Kehrmann and Bauer (Abstr., 1897, i, 27); the acetyl derivative crystallises from alcohol, and melts at 148° (these authors gave 146°). T. M. L.

Nitroso-formation from Phloroglucinolmonomethyl Ether. Jacques Pollak and G. Gans (*Monatsh.*, 1902, 23, 947—957).—Since, by the action of amyl nitrite on orcinol, a mononitroso-orcinol results with the nitroso-group between the two hydroxyls (Henrich, Abstr., 1897, i, 404; 1901, i, 464), the question is raised as to whether the nitroso-group could be introduced into phloroglucinol monomethyl ether in an analogous manner. The authors prove that the nitroso-group takes up a para-position towards one of the hydroxyl groups, by reducing the nitroso-compound and then oxidising the resulting aminophenol, when 3-hydroxy-5-methoxy-*p*-quinone was obtained.

3-*Hydroxy*-5-*methoxy*-p-*quinone*-4-*monoxime*, prepared from phloroglucinol monomethyl ether and amyl nitrite, forms dark red needles easily soluble in alcohol and insoluble in water; the *potassium* and *silver* salts are well defined. By its reduction with stannous chloride, 4-*amino*-3-*hydroxy*-5-*methoxyphenol hydrochloride* was formed; its *tetra-acetyl* derivative melts at 127—129°. When treated with carbamide, *carbonyl*-4-*amino*-1-*hydroxy*-5-*methoxyphenol* was obtained, which, on being warmed, gradually decomposed. When the hydrochloride was oxidised by ferric chloride, it yielded 3-*hydroxy*-5-*methoxy*-p-*quinone*, the *monoacetyl* derivative of which melted at 275—278°. When the quinone was reduced by stannous chloride, an oil resulted, which, on acetylation, yielded needles of the *triacetyl* derivative of 3-*hydroxy*-5-*methoxyquinol*. A. McK.

Condensations with Aminobenzyl Alcohols. Paul Friedländer (*Monatsh.*, 1902, 23, 973—1002).—[With B. von Horváth.]—When resorcinol and *p*-aminobenzyl alcohol are heated with dilute

sulphuric acid, 4'-*amino*-2 : 4-*hydroxydiphenylmethane*,

$$C_6H_3(OH)_2 \cdot CH_2 \cdot C_6H_4 \cdot NH_2,$$

is formed; it melts at 160—161°, forms salts with acids, but has also slightly acid properties, since carbon dioxide causes its precipitation from a solution in sodium hydroxide. The sparingly soluble *diaminodibenzylresorcinol sulphate* is obtained as a by-product in the preceding preparation, and from it the free base, $C_6H_2(OH)_2(CH_2 \cdot C_6H_4 \cdot NH_2)_2$, melting at 212—213° was prepared. p-*Aminophenyl-α-hydroxynaphthylmethane*, $OH \cdot C_{10}H_6 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$, prepared from α-naphthol and *p*-aminobenzyl alcohol, melts at 174—175°; it is soluble in alkali and can be diazotised. Its *acetyl* derivative melts at 124—126°.

o-Aminobenzyl alcohol is more stable than its *p*-isomeride, and its tendency to condense with phenols is less marked. 6'-*Amino*-2 : 4-*hydroxydiphenylmethane*, prepared from it and resorcinol, crystallises from water in yellowish needles, melting at 158—159°. 6'-*Amino*-2 : 4 : 6-*hydroxydiphenylmethane*, prepared in like manner from phloroglucinol, forms white needles which quickly oxidise on exposure to air.

By the action of formaldehyde on methylaniline, monomethyl-*p*-aminobenzyl alcohol is most probably first produced, but the final product is the *anhydro*-derivative, $\begin{array}{l} CH_2-C_6H_4 \cdot NMe \\ | \qquad\qquad\quad | \\ NMe \cdot C_6H_4 \cdot CH_2 \end{array}$, which forms lustrous crystals, melting at 205—210°, and giving methyl-*p*-toluidine on reduction with zinc dust. From ethylaniline, the corresponding *ethyl* compound, crystallising in long, colourless needles and melting at 79—80°, may be formed. The condensation of resorcinol, α-naphthol, and other alcohols with those anhydro-derivatives was accordingly studied.

4'-*Methylamino*-2 : 4-*hydroxydiphenylmethane* forms lustrous, pale rose-coloured crystals, melts at 111—112°, and is soluble in alkalis and in dilute mineral acids. A substance with the formula $C_{22}H_{24}O_2N_2$ is obtained as a by-product in the preceding condensation; it forms pale rose-coloured leaflets and melts at 174—175°.

4'-*Ethylamino*-2 : 4-*hydroxydiphenylmethane* crystallises in rose-coloured needles and melts at 154—155°. The by-product, $C_{24}H_{28}O_2N_2$, obtained at the same time, forms lustrous plates and melts at 101°.

p-*Methylaminophenyl-α-hydroxynaphthylmethane* crystallises from benzene in colourless prisms melting at 141—142°. The analogous *ethylamino*-compound crystallises in colourless prisms and melts at 169°.

p-*Methylaminophenyl-β-hydroxynaphthylmethane*, obtained from β-naphthol and anhydro-*p*-methylaminobenzyl alcohol, crystallises from benzene in white prisms melting at 142°. The analogous *ethylamino*-compound forms colourless needles melting at 99—100°. p-*Methylaminophenyl*-2 : 7-*dihydroxynaphthylmethane*, from 2 : 7-dihydroxynaphthalene and anhydro-*p*-methylaminobenzyl alcohol, crystallises from xylene in colourless needles melting at 179—180°. The corresponding *ethylamino*-compound melts at 153—154°.

p-*Methylaminophenyl*-2 : 3-*dihydroxynaphthylmethane*, prepared from 2 : 3-dihydroxynaphthalene, crystallises from xylene in yellowish-brown prisms melting at 185—186°. A. McK.

Synthesis of Aromatic Nitriles from Benzenoid Hydrocarbons by means of Mercury Fulminate and Aluminium Chloride. ROLAND SCHOLL (*Ber.*, 1903, 36, 10—15).—Whereas a mixture of crystalline hydrated and anhydrous aluminium chlorides in a proportion corresponding with the formula Al_2OCl_4 converts a mixture of benzene and mercury fulminate into benzaldoxime (Abstr., 1900, i, 144), dry aluminium chloride, under suitable conditions, gives rise to 80 per cent. of the theoretical quantity of benzonitrile. In the case of homologues of benzene, mixtures of the ortho- and para-derivatives are formed, which are separated only with difficulty.

As aluminium chloride does not convert benzaldoxime into benzonitrile either in boiling benzene or carbon disulphide solution, the formation of a nitrile in this synthesis cannot be due merely to the dehydrating action of dry aluminium chloride on an oxime initially formed. As cyanogen chloride is always produced in the nitrile synthesis, it appears probable that the latter occurs thus: (1) $C\!:\!N\cdot OH \rightarrow CN\cdot Cl$; (2) $CN\cdot Cl + C_6H_6 \rightarrow C_6H_5\cdot CN + HCl$.

In this paper, the formation of benzonitrile from benzene and of *o*- and *p*-tolunitriles from toluene is described. W. A. D

Formation of Aldoximes from the Homologues of Benzene by means of Mercury Fulminate and Aluminium Oxychloride. ROLAND SCHOLL and F. KAČER (*Ber.*, 1903, 36, 322—331). —Whilst benzene, mercury fulminate, and sublimed aluminium chloride yield only benzonitrile (see preceding abstract), a mixture of nitrile and benzaldoxime is obtained when water and aluminium hydroxide are present in the aluminium chloride (Abstr., 1900, i, 144). It is suggested that the sublimed aluminium chloride and the crystalline chloride containing water react to form aluminium oxytetrachloride, Al_2OCl_4, or aluminium oxychloride, AlOCl.

o- and *p*-Tolualdoximes were obtained mixed with a much smaller quantity of toluonitrile by treating toluene with mercury fulminate and aluminium chloride containing small quantities of the hydrated chloride and aluminium hydroxide; the aldoximes, which are in the *syn*-form, are separated from the nitrile by means of alkali; by this treatment, they are converted into the *anti*-form, which is stable towards alkalis; the *o*- and *p*-tolualdoximes are separated by dissolving the sodium salts in alcohol and adding ether, when the para-derivative is precipitated (m. p. 79°; Hantzsch, Abstr., 1894, i, 330); the ortho-derivative (m. p. 49°; Dollfus, Abstr., 1892, i, 1174) was purified by fractional precipitation from its ethereal solution with ethereal hydrogen chloride.

From *m*-xylene, a mixture of aldoxime and nitrile is obtained when the proportion of aluminium chloride is somewhat larger than in the case of toluene. m-*Xylyl*-4-*aldoxime*, $C_6H_3Me_2\cdot CH\!:\!NOH$, is separated from the nitriles by taking advantage of its solubility in solutions of the alkalis; the *syn*-form is purified by precipitation from its ethereal

solution by hydrogen chloride, and then converted into the *anti*-form by warming under water; the latter isomeride forms crystals melting at 85—86°, and is converted into 2 : 4-dimethylbenzoic acid (m. p. 124—125°) by heating with 75 per cent. sulphuric acid; the *syn*-aldoxime, obtained in the usual way from the *anti*-aldoxime, crystallises in needles melting at 126°. The nitriles consisted of a mixture of 2 : 6 and 2 : 4-dimethylbenzonitriles; the former separated from the oily mixture in prismatic crystals (m. p. 90—91°; Noyes, Abstr., 1899, i, 284), and was converted into 2 : 6-dimethylbenzoic acid (m. p. 116°); 2 : 4-dimethylbenzonitrile was isolated by fractionating the remaining oil, and was converted into the corresponding dimethylbenzoic acid (m. p. 124°).

From *o*-xylene, o-*xylyl*-4-*aldoxime* was obtained in the *anti*-form in a manner similar to that just described; it melts at 106° and yields a *sodium* salt crystallising in scales; by treatment with sulphuric acid, it gives 3 : 4-dimethylbenzoic acid (m. p. 163°). The *syn*-form of the aldoxime could not be prepared. 3 : 4-*Dimethylbenzonitrile* is obtained as the last fraction when the mixture of this compound with 2 : 3-dimethylbenzonitrile is distilled in steam; it melts at 66° and is not an oil, as Kreysler (Abstr., 1885, 1055) has stated; on hydrolysis with sulphuric acid, 3 : 4-dimethylbenzoic acid is produced. The isomeric 2 : 3-dimethylbenzonitrile is contained in the first oily fraction of the steam distillation; this was fractionated, and the liquid boiling between 200—230° converted into the acid, from which 2 : 3-dimethylbenzoic acid (m. p. 142—143°) was isolated.

p-*Xylyl*-2-*aldoxime* was obtained directly in the *syn*-form from the mixture of aldoxime and nitrile prepared from *p*-xylene; it crystallises in slender needles melting at 139°, and is easily changed into the *anti*-form melting at 60°; 2 : 5-dimethylbenzonitrile, prepared by fractionating the oily residue from which the aldoxime has been extracted by alkali, forms crystals melting at 5·5°, and yields 2 : 5-dimethylbenzoic acid (m. p. 132°) on hydrolysis.

syn-Mesitylaldoxime (m. p. 180—181°; Hantzsch and Lucas, *loc. cit.*, give the melting point as 179°) separates from the mixture of aldoxime and nitrile prepared from mesitylene; the *anti*-form, obtained from the *syn*-form, melts at 124°. The nitrile was isolated from the oily residue in crystals melting at 53°. K. J. P. O.

[Chloro- and Bromo-hippuric Acids.] HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1902, 3, 365—372). See this vol., ii, 228.

***iso*Cinnamic Acid.** CARL LIEBERMANN [and, in part, B. HALVORSEN] (*Ber.*, 1903, 36, 176—183).—Owing to Michael's recent publication (Abstr., 1902, i, 32), in which the preparation of a mixture of *allo*- and *iso*-cinnamic acids by reduction of β-bromo*allo*cinnamic acid is described, the isolation of *iso*cinnamic acid from the mixture of acids obtained in the manufacture of quinine has been again undertaken (compare Liebermann, Abstr., 1890, 494, 620, and 1417). A very large quantity (2·5 kilos). of the mixed acids, which in this case was rich in *allo*cinnamic acid, was worked up. The mixed acids were freed from benzoic acid by distillation with steam, and the residue, after dissolving

in ether and drying, was allowed to solidify slowly ; the crystals were removed continually as they formed, and the remaining oil allowed to solidify further. The oily residue finally obtained was converted into barium salt, which was recrystallised from a small quantity of methyl alcohol in the manner described by Michael (*loc. cit.*). From the barium salt thus purified, *allo*cinnamic acid was always obtained, together with an oil which only slowly solidified and then showed a very uncertain melting point, certain fractions giving the melting point observed by Michael for his *iso*cinnamic acid (m. p. 37°), which was 20° lower than that originally found by the author. No acid could be isolated which was free from *allo*cinnamic acid. Reinvestigation has also shown that barium *allo*cinnamate crystallises with H_2O, and not with $3H_2O$, as Michael states; further, this salt dissolves at 19° in 5 parts of methyl alcohol, and not in 38 parts (Michael), the presence of other barium salts, such as barium benzoate, greatly increasing the solubility. Calcium *allo*cinnamate crystallises with $2H_2O$ (compare Michael) and dissolves in 9·8 parts of water at 20°. In the first paper (Liebermann, *loc. cit.*), it was stated that *allo*cinnamic acid was much less soluble in petroleum (b. p. 60°—70°) than *iso*cinnamic acid ; it is found, however, that in the presence of 10 per cent of benzoic acid one part of *allo*cinnamic acid dissolves in 13 parts of petroleum, whereas one part of the pure acid dissolves in 49·2—51·8 parts. Recent determinations of the electrical conductivity made by Ostwald show that pure *allo*cinnamic acid has K 0·0162 ; the value for *iso*cinnamic acid, determined in 1890, was 0·0158. The crystallographic differences, on which stress was previously laid, have also largely disappeared, as renewed investigation has shown that *allo*cinnamic acid, in a state of undoubted purity, exhibits many of the forms previously thought to be characteristic of *iso*cinnamic acid. It seems, then, highly probable that *iso*cinnamic acid does not exist. K. J. P. O.

Triphenylacetic Acid from Chlorodiphenylacetic Acid. AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1903, **36**, 145—147).—*Chlorodiphenylacetic acid*, $CPh_2Cl\cdot CO_2H$, may be prepared by gently heating benzilic acid with phosphorus oxychloride, and crystallises in rhombic tablets which melt and decompose at 118—119°. When it is heated with benzene and aluminium chloride, it yields 25 per cent. of the theoretical amount of triphenylacetic acid. A. H.

Mercury Salicylate. G. BURONI (*Gazzetta*, 1902, **32**, ii, 311—313).—The compound obtained by mixing solutions of mercuric acetate and sodium salicylate, and stated by Goepel (*Chem. Zeit. Rep.*, 1889, 107) to be mercury salicylate, is shown by the author to contain more than the proper proportion of mercury, due, probably, to the formation of some basic salicylate.

Mercury salicylate is, however, obtained pure if a solution of mercuric acetate is added to a solution of sodium salicylate acidified with acetic acid. The salt readily changes, especially when not quite dry or when heated, into oxymercurisalicylic anhydride and salicylic acid. T. H. P.

Action of Bromine on *m*-Hydroxybenzoic Acid. ANGELO COPPADORO (*Gazzetta*, 1902, **32**, ii, 332—339).—6-*Bromo-3-hydroxybenzoic acid*, prepared by the action of bromine (1 mol.) on *m*-hydroxybenzoic acid (1 mol.) in acetic acid solution, crystallises from water in acicular flocks melting at 221°; the *methyl* ester separates from aqueous alcohol in needles and melts at 126°; the *ethyl* ester melts at 94°.

By the action of 2 mols. of bromine on *m*-hydroxybenzoic acid in acetic acid solution, the following three acids are obtained: (1) 6-bromo-3-hydroxybenzoic acid; (2) 2 : 4 : 6-tribromo-3-hydroxybenzoic acid, already prepared by Werner (Abstr., 1886, 1015) and by Krause (Abstr., 1899, i, 281); and (3) 4 : 6-*Dibromo-3-hydroxybenzoic acid*, which separates from aqueous solution in crystals melting at 194—195°, and yields a *methyl* ester melting at 144—145°. T. H. P.

New Drugs. III. Methyl *m*-Amino-*p*-hydroxybenzoate ("Orthoform neu"). ALFRED EINHORN and EDUARD RUPPERT (*Annalen*, 1902, **325**, 305—339. Compare Abstr., 1900, i, 439, 493).—Methyl *m*-amino-*p*-hydroxybenzoate is generally obtained in the form of slender needles melting at 142°, but it has also been observed to crystallise in prisms melting at 110—111° (Auwers and Rohrig, Abstr., 1897, i, 341). It has been found that this form of low melting point ("orthoform neu") can easily be prepared by adding a few drops of ethylenediamine to an aqueous solution of the ordinary form, when it separates in lustrous, quadratic leaflets melting at 110—111°. It gives an intense red solution in nitric acid, and is thus distinguishable from the corresponding pseudo-form of methyl *p*-amino-*m*-hydroxybenzoate, which gives a dark green solution with this acid. A large number of salts and derivatives of these pseudo-forms are described in the paper.

The *hydrochloride* of the pseudo-form of methyl *m*-amino-*p*-hydroxybenzoate crystallises in slender needles melting and decomposing at 225°, and in aqueous solution gives a red coloration with ferric chloride; the *hydrobromide* forms small needles melting and decomposing at 232°; the *nitrate* and *sulphate* crystallise in needles; the *compound* with mercuric chloride, $C_8H_9O_3N,HgCl_2$, prepared by shaking up the ester with a solution of mercuric chloride, crystallises in yellow needles melting at 165°, and with warm water decomposes, mercuric oxide and mercury being formed. The *mercurichloride*, $C_8H_9O_3N,HHgCl_3,H_2O$, prepared by mixing solutions of the ester and mercuric chloride, crystallises in pale red needles melting at 185°; the *zincochloride*, $(C_8H_9O_3N,HCl)_2,ZnCl_2$, forms colourless needles melting at 243°; the *platinichloride* crystallises in yellow needles melting at 225°.

With antipyrine, the *o*-aminophenols yield additive compounds which are possibly of the nature of betaines. The *compound* of antipyrine with methyl *p*-amino-*m*-hydroxybenzoate, $C_8H_9O_3N,C_{11}H_{13}ON_2$, is prepared by mixing its two constituents in ethyl acetate solution; it crystallises in large, yellow, twinned, monoclinic prisms [$a:b:c=$ 1·1580 : 1 : 0·5343]. The corresponding *additive* compound from antipyrine and methyl *m*-amino-*p*-hydroxybenzoate forms colourless, tri-

clinic crystals melting at 93° and is decomposed into its constituents by hydrochloric acid. An *additive* compound ("salipyrin-orthoform"), $C_{26}H_{27}O_7N_3$, prepared by melting mol. proportions of antipyrine, salicylic acid, and methyl *p*-amino-*m*-hydroxybenzoate together at 140—160°, crystallises from toluene in yellowish plates melting at 76°, and is decomposed by hydrochloric acid into its components. The corresponding *compound* from methyl *m*-amino-*p*-hydroxybenzoate ("salipyrin-orthoform neu") crystallises in prismatic needles melting at 75—77°. The *additive* compound ("tolypyrin-orthoform") obtained on melting together 1-*p*-tolyl-2 : 3-dimethyl-5-pyrazolone and methyl *p*-amino-*m*-hydroxybenzoate at 140°, crystallises in small, white prisms melting indefinitely at 86°, whilst the *isomeride*, prepared in a similar manner from methyl *m*-amino-*p*-hydroxybenzoate, forms lustrous plates melting at 79—80°. On melting together 4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone and methyl *p*-amino-*m*-hydroxybenzoate, an *additive* compound is formed which crystallises in rhombic plates melting at 76°; the corresponding derivative of methyl *m*-amino-*p*-hydroxybenzoate forms prisms melting at 65—66°. *Methyl* m-*acetylamino*-p-*hydroxybenzoate*, prepared by boiling a benzene solution of the ester with acetyl chloride, crystallises in small needles melting at 198°. *Methyl* m-*phenylsulphonamino*-p-*hydroxybenzoate*,

$$SO_2Ph\cdot NH\cdot C_6H_3(OH)\cdot CO_2Me,$$

prepared by the action of benzenesulphonic chloride on a pyridine solution of the ester, crystallises in small needles melting at 197°. *Methyl* m-*carbamino*-p-*hydroxybenzoate*, prepared from the hydrochloride of the ester and potassium cyanate, forms small, prismatic crystals melting at 185°. *Methyl* m-*thiocarbamino*-p-*hydroxybenzoate*, prepared in a similar manner by use of potassium thiocyanate, crystallises in prismatic needles melting at 163°.

Ethyl chloroacetate and methyl *m*-amino-*p*-hydroxybenzoate yield, with elimination of hydrogen chloride, *methyl ethyl* m-*carboxy*-o-*hydroxyphenylaminoacetate*, $CO_2Et\cdot CH_2\cdot NH\cdot C_6H_3(OH)\cdot CO_2Me$, which crystallises with alcohol in needles melting at 99—100°, or when free from alcohol at 126°. *Methyl ethyl* m-*carboxyamino*-p-*hydroxybenzoate*, $CO_2Et\cdot NH\cdot C_6H_3(OH)\cdot CO_2Me$, is prepared from ethyl chlorocarbonate and the ester; it crystallises in needles melting at 158°. The corresponding *acid*, prepared by boiling the ester with sodium hydroxide, forms yellow needles which do not melt at 280°. When the ester is heated for a short time at 180°, alcohol is eliminated, and *methyl carbonyl*-m-*amino*-p-*hydroxybenzoate*, $CO<{NH \atop O}>C_6H_3\cdot CO_2Me$, is formed; it crystallises in needles melting at 196·5°.

When heated together in ethereal solution, catechol carbonate and methyl *m*-amino-*p*-hydroxybenzoate yield the catechol ester of the carbamic acid, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot C_6H_3(OH)\cdot CO_2Me$; it crystallises in small needles melting at 161°, and very readily decomposes into the carbonyl derivative just described and catechol.

Methyl m-*dimethylaminoanisate*, $NMe_2\cdot C_6H_3(OMe)\cdot CO_2Me$, is obtained in the form of a methiodide when methyl *m*-amino-*p*-hydroxybenzoate, methyl iodide, and potassium hydroxide are left in alcoholic solution; it crystallises in white needles melting at 206°, and yields

trimethylanisobetaine and methyl *m*-dimethylaminoanisate when successively treated with lead hydroxide and distilled (Griess, this Journal, 1873, 1145); the *hydriodide* of methyl *m*-diaminoanisate melts at 177°. *Methyl* m-*methyl-* and m-*dimethyl-amino*-p-*hydroxybenzoate*, $NHMe\cdot C_6H_3(OH)\cdot CO_2Me$, are formed when the ester and methyl iodide are heated together in alcoholic solution; the mixture is separated into its components by treating with catechol carbonate, which forms, with the monomethyl derivative, the carbonyl derivative, $CO<\overset{NMe}{\underset{O}{}}>C_6H_3\cdot CO_2Me$; the latter crystallises in lustrous needles melting at 168°; when heated with hydrochloric acid, the substance last mentioned is converted into m-*methylamino*-p-*hydroxybenzoic acid*, $NHMe\cdot C_6H_3(OH)\cdot CO_2H$, which crystallises in yellowish needles melting at 190°; the *hydrochloride* forms crystals melting at 220°. From this acid, *methyl* m-*methylamino*-p-*hydroxybenzoate* is easily prepared in the usual way; it crystallises in needles melting at 154°. The dimethylamino-derivative, prepared as above described, crystallises from dilute alcohol in monoclinic prisms melting at 59·5—60°, and with ferric chloride gives a violet coloration; the *hydrochloride* forms small needles melting at 176°, and the *platinichloride* yellow needles melting at 197°; the *methiodide* crystallises in star-shaped aggregates of needles melting at 190°. By the action of ethyl iodide on methyl *m*-amino-*p*-hydroxybenzoate, a mixture of *ethyl* and *diethyl* derivatives is obtained; these are separated by treatment with carbonyl chloride; this converts the monoethyl derivative into an insoluble carbonyl compound melting at 105°, from which the ethylamino-derivative can be prepared in the same manner as the methylamino-derivative; it crystallises in needles melting at 117°, and yields a *hydrochloride* melting at 210°. *Methyl* m-*diethylamino*-p-*hydroxybenzoate* is purified by conversion into the *hydrobromide*, which crystallises in needles melting at 202°; the base is an oil boiling at 285° and solidifying below 0°; the *hydriodide* is formed when the amino-ester is treated with ethyl iodide and potassium hydroxide in dilute alcoholic solution; it crystallises in small, white needles melting at 188°.

When chloroacetic acid is heated with methyl *m*-amino-p-hydroxybenzoate at 150—160°, methyl *m*-chloroacetylamino-*p*-hydroxybenzoate (Einhorn and Oppenheimer, Abstr., 1900, i, 493) is produced; if excess of the ester is used, *methyl* 1′-*carboxy*-4′-*hydroxy*-3′-*acetanilino*-1-*carboxy*-4-*hydroxy*-3-*anilide*,

$$CO_2Me\cdot C_6H_3(OH)\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3(OH)\cdot CO_2Me,$$

is formed; it crystallises in small groups of needles melting at 219°, and gives with ferric chloride a deep green coloration; if the ester and the chloroacetic acid are heated together at a higher temperature, 190°, a monobasic acid, $C_{17}H_{16}O_7N_2$, is obtained as an insoluble powder, not melting at 280°; it is probably the acid ester, of which the compound just described is the di-ester. When methyl *m*-amino-*p*-hydroxybenzoate reacts with chloroacetic acid in the presence of sodium carbonate, *methyl* 6-*carboxy*-2-*ketophenomorpholine*-4-*acetic acid*, $CO_2Me\cdot C_6H_3<\overset{O\text{———}CO}{\underset{N(CH_2\cdot CO_2H)}{}}>CH_2$, is formed; it crystallises from

ethyl acetate in lustrous scales melting at 227°, and gives a red coloration with ferric chloride; the *ester* is formed on boiling the acid with alcohol; it crystallises in silky needles melting at 136° and gives no coloration with ferric chloride.

Methyl o-*nitro*-p-*carboxyphenoxyacetamide*,

$$NH_2\cdot CO\cdot CH_2\cdot O\cdot C_6H_3(NO_2)\cdot CO_2Me,$$

is produced when mol. proportions of chloroacetamide and the potassium salt of methyl *m*-nitro-*p*-hydroxybenzoate are fused at 180°; the ester crystallises in needles melting at 186°. On reduction with aluminium amalgam, *methyl* m-*amino*-p-*carboxyphenoxyacetamide* is obtained, crystallising in silky needles melting at 178°; when dissolved in mineral acids, it is converted into methyl 3-ketophenomorpholine-6-carboxylate (m. p. 193°). The latter substance is also formed when the ester is heated at 190°, ammonia being eliminated. If the nitro-compound is reduced in acid solution, the same ketophenomorpholine is formed, together with an *acid*, $C_{10}H_{11}O_5N$, which crystallises in needles melting at 191°, and with ferric chloride gives a violet coloration; its *benzoyl* derivative, $C_{10}H_{10}O_5NBz$, forms lustrous leaflets melting at 138°. K. J. P. O.

Action of *p*-Nitrobenzyl Chloride on Acetoacetic and Cyanoacetic Esters and their Derivatives. G. Romeo (*Gazzetta*, 1902, 32, ii, 355—364).—The interaction of *p*-nitrobenzyl chloride and ethyl acetoacetate in absolute alcoholic solution in presence of sodium gives rise to: (1) Dinitrostilbene. (2) *Ethyl di*-p-*nitrodibenzylacetoacetate*, $CAc(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot CO_2Et$, which is soluble in benzene or alcohol, being deposited from the latter solvent in small, colourless, shining scales melting at 139—140°. (3) *Ethyl di*-p-*nitrodibenzylacetate*, $CH(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot CO_2Et$, which is soluble in light petroleum, benzene, or alcohol, from the last of which it crystallises in colourless, shining needles melting at 106—107°.

Ethyl di-p-*nitrodibenzylcyanoacetate*, $CN\cdot C(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot CO_2Et$, prepared from *p*-nitrobenzyl chloride and ethyl cyanoacetate, is soluble in benzene or acetic acid, from the latter of which it is deposited in colourless, triclinic crystals melting at 164—165°.

Di-p-*nitrodibenzylcyanoacetamide*, $CN\cdot C(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot CO\cdot NH_2$, obtained by the action of *p*-nitrobenzyl chloride on cyanoacetamide, dissolves slightly in alcohol and to a greater extent in acetic acid, from which it crystallises in elongated, colourless laminæ melting at 230—231°.

Di-p-*nitrodibenzylmalonitrile*, $C(CH_2\cdot C_6H_4\cdot NO_2)_2(CN)_2$, prepared by heating the preceding compound, or, together with ethyl di-*p*-nitrobenzylcyanoacetimino-ether, by the interaction of sodium, *p*-nitrobenzyl chloride, and malonitrile (dicyanomethane), dissolves slightly in alcohol or benzene, more readily so in acetic acid, from which it crystallises in bundles of flattened needles melting at 219—221°.

Ethyl di-p-*nitrodibenzylcyanoacetoimino-ether*,

$$CN\cdot C(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot C(NH)\cdot OEt,$$

obtained as above or by the interaction of malonitrile and *p*-nitrobenzyl chloride in absolute alcohol in presence of sodium, crystallises from alcohol or benzene in minute, colourless needles melting at 169—170°.

T. H. P.

Acenaphthenequinone. Vincenzo Recchi (*Gazzetta*, 1902, 32, ii, 365—369).—When acenaphthenequinone and ethyl acetoacetate in molecular proportion are condensed in presence of potassium hydroxide, they yield a *compound* having the constitution

$$C_{10}H_{16}<\begin{matrix}CO \\ | \\ C:CAc\cdot CO_2Et,\end{matrix}$$

which separates from benzene in yellow crystals melting at 150°.

If aqueous ammonia is employed as condensing agent in place of potassium hydroxide, these two substances yield a *compound*

$$C_{10}H_{16}<\begin{matrix}C:CAc\cdot CO_2Et \\ | \\ C:CAc\cdot CO_2Et'\end{matrix}$$

which crystallises from ethyl acetate in small, white laminæ melting at 174—175°. T. H. P.

Fusion of some Typical Santonin Derivatives with Potassium Hydroxide. P. Bertolo (*Gazzetta*, 1902, 32, ii, 371—379).—When fused with potassium hydroxide, desmotroposantonin, *iso*desmotroposantonin, *l*-desmotroposantonin, and *d*-desmotroposantonin all yield the 1 : 3-dimethyl-β-naphthol obtained in the same way by Andreocci (Abstr., 1896, i, 182) from the santonous acids. Under the same conditions, 1 : 3-dimethylnaphthalene is obtained from hypo*iso*santonin, but santonin, santonic acid, santonone, and *iso*santonone, when fused with potassium hydroxide, yield no definite product.

The following conclusions are drawn : (1) All derivatives of santonin in which the ketonic group, $-CH_2\cdot CO\cdot$, is converted into the phenolic group, $-CH:C(OH)\cdot$, when fused with potassium hydroxide yield 1 : 3-dimethyl-β-naphthol as the principal product. (2) Those derivatives in which the ketonic is reduced to the methinic group, $-CH:CH\cdot$, give an almost theoretical yield of the corresponding hydrocarbon, 1 : 3-dimethylnaphthalene. (3) Derivatives which, like santonin, retain the ketonic group, yield neither the naphthol nor the hydrocarbon, but form decomposition products precipitable by dilute sulphuric acid. T. H. P.

Benzyl Esters of Carbonic and Phthalic Acids. Carl A. Bischoff (*Ber.*, 1903, 36, 159—161. Compare Abstr., 1903, i, 26).—Sodium benzoate is formed as an impurity in the preparation of sodium benzyloxide if the action be prolonged or if the temperature be too high. Dibenzyl carbonate, prepared from sodium benzyloxide and carbonyl chloride, boils at 195—203° under 12 mm. pressure, and solidifies forming prisms melting at 29°.

The monobenzyl phthalate previously described by the author is identical with the substance obtained by Meyer (Abstr., 1897, i, 350) from silver phthalate and moist benzyl iodide.

Dibenzyl carbonate is not decomposed by phenol, and hence this substance cannot be assumed to be an intermediate product in the formation of phenyl benzyl ether by the action of benzyl alcohol on phenyl carbonate. A. H.

Derivatives of Dichlorophthalic Acid. ÉMILE C. SEVERIN (*Bull. Soc. chim.*, 1903, [iii], **29**, 60—62).—*2′-Dimethylamino-3′-hydroxybenzoyl-3 : 6-dichlorobenzoic acid*, $NMe_2 \cdot C_6H_3(OH) \cdot CO \cdot C_6H_2Cl_2 \cdot CO_2H$, obtained by melting together *m*-dimethylaminophenol and dichlorophthalic anhydride [D.R.P. 87068], separates from alcohol in colourless crystals, melts at 191°, and when heated with *m*-dimethylaminophenol dissolved in sulphuric acid, furnishes the *rhodamine*,

$$C_6H_2Cl_2[CO \cdot C_6H_3(OH) \cdot NMe_2]_2,$$

which forms small, violet crystals, and dyes silk in red tints with a violet shade. When condensed with *m*-diethylaminophenol, the corresponding mixed *rhodamine* is produced, but has not been obtained pure.

2′-Dimethylamino-3′-hydroxybenzyl-3 : 6-dichlorobenzoic acid, prepared by reducing the foregoing, is a colourless, crystalline substance, which melts at 195°.

5 : 8 : 1-*Dimethylamino-2-hydroxydichloroanthraquinone*, obtained by heating 2′-dimethylamino-3′-hydroxybenzoyl-3 : 6-dichlorobenzoic acid with sulphuric acid at 100°, separates from acetic acid in violet flakes with a bronze lustre and melts at 185°. T. A. H.

New Reagent for Inducing the Hofmann Reaction. JOSEPH TSCHERNIAC (*Ber.*, 1903, **36**, 218).—Phthalimide is readily transformed into anthranilic acid when shaken with alkali and iodosobenzene. The iodosobenzene plays the part of the alkali hypochlorite in the ordinary Hofmann transformation of acid amides into amines. No isatoic acid is formed when only one equivalent of alkali is employed. J. J. S.

Methylgallic Acids and Synthesis of Syringic Acid. CARL GRAEBE and E. MARTZ (*Ber.*, 1903, **36**, 215—217).—*Gallic acid methyl ether* $[CO_2H : (OH)_2 : OMe = 1 : 3 : 5 : 4]$ is readily obtained when gallic acid is dissolved in sodium hydroxide solution (2 mols.) and warmed with methyl sulphate. It melts at 240°, dissolves readily in hot water, but is insoluble in chloroform. Its *methyl* ester,

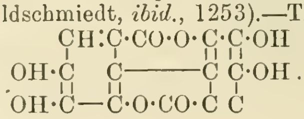
$$OMe \cdot C_6H_2(OH)_2 \cdot CO_2Me,$$

crystallises from a mixture of chloroform and light petroleum in needles melting at 147·5°.

Syringic acid, $OH \cdot C_6H_2(OMe)_2 \cdot CO_2H$ $[CO_2H : OH : (OMe)_2 = 1 : 4 : 3 : 5]$, is obtained when gallic acid trimethyl ether is hydrolysed with concentrated hydrochloric acid (5 parts) at 100°.

Its methyl ester crystallises with H_2O; when hydrated, it melts at 83—84°; when anhydrous, at 106°. J. J. S

Constitution of Ellagic Acid. CARL GRAEBE (*Ber.*, 1903, **36**, 212—215. Compare H. Schiff, *Ber.*, 1879, **12**, 1534; Barth and Goldschmiedt, *ibid.*, 1253).—The constitution of ellagic acid is given as



. The fact that fluorene is formed when

the acid is distilled with zinc dust cannot be used as an argument against such a formula, as it is now shown that diphenylmethylolide, $\begin{array}{l}C_6H_4{\cdot}CO \\ | \quad\quad | \\ C_6H_4{\cdot}O\end{array}$, also yields a small amount of fluorene in addition to diphenyl and 2-methyldiphenyl. J. J. S.

Racemic Nature of *i*-Usnic Acid. ANDREAS SMITS (*Annalen*, 1902, **325**, 339—347).—As a result of his observations on usnic acid from various sources, Widman (Abstr., 1900, i, 235, 347) stated that both *d*- and *l*-usnic acids melted at 203°, whereas *i*-usnic acid melted at 191—192°. Salkowski (Abstr., 1901, i, 152), on the other hand, found that active and inactive usnic acids exhibited melting points which varied between 192° and 202°. When the melting point is taken with a delicate thermometer dipped into the molten substance, the melting point of either *d*- or *l*-usnic acid is 191·4°, and that of *i*-usnic acid 193°. The observations of the authors above mentioned are possibly explained by the fact that both *d*- and *l*-usnic acids can be heated to 196° without melting; when melting sets in, the temperature sinks to 191·4°. *i*-Usnic acid does not behave in this manner. The relation of these melting points makes it very probable that *i*-usnic acid is a true racemic compound at its melting point. The melting points of eutectic mixtures of benzoin and the usnic acids show that this is the case at 127°, the melting point of this mixture. The eutectic mixture of benzoin and *d*-usnic acid, which contains 29 per cent. of the acid, melts at 127·3°, a mixture of the same composition of *i*-usnic acid and benzoin melting at 128°. Both *d*- and *l*-usnic acids illustrate to a remarkable degree the fact that velocity of crystallisation is dependent on temperature. When the molten acids are cooled rapidly, they form amorphous gums which will not crystallise until they are again heated in the neighbourhood of their melting point.

K. J. P. O.

Reduction of some Aromatic Nitro-compounds. FREDERICK ALWAY and M. D. WELSH (*J. Amer. Chem. Soc.*, 1902, **24**, 1052—1060). —*m*- and *p*-Nitrobenzaldehydes, when reduced by zinc dust, form substances of an unknown nature, which, on oxidation, yield nitrosobenzaldehydes. By reduction with zinc dust in presence of ammonium chloride, the authors obtained various condensation products of the hydroxylaminobenzaldehydes, but neither of the corresponding *N*-formylphenyl ethers of the nitrobenzaldoximes was detected, however, although they are formed in the electrolytic reduction (Gattermann, Abstr., 1897, i, 189). The insoluble compound obtained by Bamberger and Friedman (*Ber.*, 1895, 28, 250) from *m*-nitrobenzaldehyde has probably the formula $O{<}{\begin{array}{l}N{\cdot}C_6H_4{\cdot}CH\\CH{\cdot}C_6H_4{\cdot}N\end{array}}{>}O$. *p*-Nitrobenzaldehyde forms a similar compound together with one or more insoluble condensation products derived from *p*-hydroxylaminobenzaldehyde. E. F. A.

Citronellaldoxime and its Transformation Product. FRIEDRICH MAHLA (*Ber.*, 1903, 36, 484—490. Compare Tiemann and Krüger, Abstr., 1896, i, 384).—Tiemann and Krüger's amino-4-menthone is presumably Δ^{8}-*hydroxylamino-3-menthene*,

$$CHMe<\begin{matrix}CH_2\cdot CH(NH\cdot OH)\\ CH_2\text{———————}CH_2\end{matrix}>CH\cdot CMe{:}CH_2.$$

It distils at 122—123° under 14 mm. pressure, has a sp. gr. 0·9736, n_D 1·47877, and a rotation of $-3°$ in a 10 cm. tube at 25°. Its strong reducing properties are more in harmony with the above formula than with that suggested by Tiemann and Krüger. The *oxalate*, $(C_{10}H_{20}ON)_2C_2O_4$, melts at 136° and dissolves readily in water or alcohol. The *benzoyl* derivative, $C_{17}H_{23}O_2N$, melts at 63°, and the *nitroso* compound, $C_{10}H_{18}O_2N_2$, at 52°, the latter exploding with violence when heated to a higher temperature.

When the nitroso-derivative is warmed with dilute sulphuric acid, it yields nitrous oxide and a hydrocarbon, $C_{10}H_{16}$, probably either $\Delta^{5,8(9)}$-*p*-menthadiene or $\Delta^{2,8(9)}$-*p*-menthadiene. This distils at 75—80° under 9 mm. pressure, has n_D 1·49824, a sp. gr. 0·8491, and a rotation of $+8·4°$ in a 10 cm. tube at 20°. It readily decolorises permanganate, combines with bromine, and dissolves sodium without the evolution of hydrogen. The hydrocarbon is always accompanied by an alcohol, $C_{10}H_{20}O$, which may be removed by Tiemann and Krüger's method as the sodium salt of its acid ester of phthalic acid. The alcohol boils at 119—125° under 19 mm. pressure and is optically active. J. J. S.

Action of Aluminium Bromide on Ketones. MICHAËL I. KONOWALOFF and FINOGUÉEFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 944—949).—Under the influence of aluminium bromide in presence of ethyl bromide, acetophenone undergoes two distinct transformations: (1) three molecules of the ketone condense, with elimination of $3H_2O$, yielding *s*-triphenylbenzene and (2) two molecules of the ketone condense forming first, possibly, a hydroxy-ketone, which loses one molecule of water, yielding *methylstilbyl phenyl ketone* ($\beta\delta$-diphenyl-Δ^{β}-buten-δ-one), CMePh:CH·COPh, as a yellow, oily liquid boiling at 340—345°, and having the sp. gr. 1·108 at 20°/0°; it has the normal molecular weight in freezing benzene, and instantly decolorises bromine or potassium permanganate; with hydroxylamine, it yields a *hydroxyamine*, $OH\cdot NH\cdot CMePh\cdot CH_2\cdot COPh$, crystallising from ether in colourless, rectangular, parallelopipedons melting at 112°.

The part played by the ethyl bromide in these condensations of acetophenone is unknown. T. H. P.

***o-p*-Dinitrobenzaldehyde. II.** PAUL FRIEDLÄNDER and PAUL COHN (*Monatsh.*, 1902, 23, 1003—1007. Compare Abstr., 1902, i, 790).—o-p-*Dinitrophenyllactyl methyl ketone*, $C_6H_3(NO_2)_2\cdot CH(OH)\cdot CH_2\cdot COMe$, prepared by the condensation of *o-p*-dinitrobenzaldehyde with acetone, crystallises in long, pale yellow prisms and melts at 63—64°. Its *phenylhydrazone* crystallises from xylene in red needles melting and decomposing at 227°. When heated with acetic anhydride, dinitrophenyllactyl methyl ketone gives *dinitrocinnamyl methyl ketone*,

$C_6H_3(NO_2)_2 \cdot CH{:}CH \cdot COMe$ [$NO_2 = 2 : 4$], crystallising from alcohol in yellow needles which melt at 73—74°. Its *phenylhydrazone* forms reddish-brown needles and melts at 191°.

Excess of sodium carbonate added to a hot aqueous solution of dinitrophenyllactyl methyl ketone causes the immediate separation of a dinitro-indigotin,

$$NO_2 \cdot C_6H_3 <\begin{smallmatrix}CO\\NH\end{smallmatrix}> C{:}C <\begin{smallmatrix}CO\\NH\end{smallmatrix}> C_6H_3 \cdot NO_2 \; [NO_2 : CO : NH = 4 : 1 : 2],$$

isomeric with the dinitro-indigotin [NO_2 : CO : NH = 5 : 1 : 2] prepared by Baeyer from nitroisatin chloride. A. McK.

Hydroxybenzylideneacetone and Dihydroxydibenzylideneacetone. Theodor Zincke and G. Mühlhausen (*Ber.*, 1903, 36, 129—134).—p-*Dihydroxydibenzylideneacetone*, $CO(CH{:}CH \cdot C_6H_4 \cdot OH)_2$, is formed, together with a small amount of hydroxybenzylideneacetone, by the condensation of acetone and *p*-hydroxybenzaldehyde in presence of hydrochloric acid. It exists in two modifications, the constitutional relations between which have not yet been made out. The *stable* form crystallises in orange-yellow plates or needles melting at 237—238°, and forms dark orange-coloured solutions in alkalis. The *acetyl* compound crystallises in yellow, silky needles melting at 165—166°. The methyl ester is identical with the dianisylideneacetone of Baeyer and Villiger (Abstr., 1902, i, 380). Dihydroxydibenzylideneacetone readily forms oxonium salts with acids. The *hydrochloride*, $C_{17}H_{14}O_3,HCl$, forms small, bluish-black, lustrous prisms, and the *hydrobromide* forms large crystals resembling those of the hydrochloride. The *sulphate*, $C_{17}H_{14}O_3,H_2SO_4$, crystallises in almost black needles with a metallic lustre. The *labile* modification of dihydroxydibenzylideneacetone is obtained by the decomposition of the hydrochloride formed in the preparation of the original condensation product, and crystallises in dark green, lustrous plates. The alcoholic solution is green and yields the green compound when immediately diluted with water. When preserved or heated, its colour changes to brown, and it then contains the stable form. When the green form is heated, it passes into the yellow, stable form at about 100—145°. The *hydrochloride* of the labile form separates in bluish-black crystals. The salts cannot be prepared in alcohol or acetone solutions, as the salts of the yellow form are then at once produced. *Hydroxybenzylideneacetone*, $OH \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot CH_3$, crystallises in long, colourless needles melting at 102—103°, and also forms coloured salts with acids. The *acetyl* compound crystallises in small, silky needles melting at 80—81°.

Both the mono- and di-hydroxy-compounds yield bromo-derivatives, which behave like true bromophenols and not, as was expected, like pseudo-bromides. A. H.

Synthetic Preparations by means of Indandione (Diketohydrindene). Giorgio Errera (*Gazzetta*, 1902, 32, ii, 330—331).—The author gives the following preliminary results of work he is obliged to postpone.

The condensation of indandione with ethyl orthoformate in presence of acetic acid does not yield the expected ethoxymethylene derivative,

the principal product of the reaction being a hydroxymethylene *compound* of the constitution $C_6H_4{<}{}^{CO}_{CO}{>}C{:}CH{\cdot}OH$, which forms hydrated, reddish crystals and yields a well-crystallised, yellow *sodium* derivative. In presence of water, this compound undergoes partial decomposition into formic acid and indandione, the latter then condensing with the unaltered compound to give *methenylbisindandione*, $C_6H_4{<}{}^{CO}_{CO}{>}C{:}CH{\cdot}CH{<}{}^{CO}_{CO}{>}C_6H_4$, which forms long, red needles only slightly soluble in the ordinary solvents and yields yellow salts with the alkali metals and a yellow oxime. With aqueous ammonia, it reacts in two ways: (1) yielding indandione and *aminomethylene-indandione*, and (2) giving *a-diphenylpyridinediketone*; both these compounds crystallise well. T. H. P.

Additive Compounds of Tetrabromo-*o*-benzoquinone. C. Loring Jackson and Horace C. Porter (*Ber.*, 1903, **36**, 454—456. Compare this vol., i, 102).—The *additive* compound, $2C_6O_2Br_4,MeOH$, is formed when tetrabromo-*o*-benzoquinone is left in contact with methyl alcohol for 8 days at the ordinary temperature; it crystallises in white, rhombic plates, melts at 261°, and is much more stable than the analogous dianilino-derivative (*loc. cit.*); with acetic anhydride, it gives an *acetyl* derivative, $C_{15}H_6O_6Br_8$, which crystallises from methyl alcohol or benzene and melts at 249°. Benzyl alcohol gives a similar compound, and when tetrabromo-*o*-benzoquinone is left in contact with ordinary moist toluene for a week, the *additive* compound, $2C_6O_2Br_4,H_2O$, separates; it crystallises from chloroform and light petroleum, and begins to decompose at 180° with the production of a red substance.
W. A. D.

The Alkylation of Anthragallol. Friedrich Böck (*Monatsh.*, 1902, **23**, 1008—1021).—For the purpose of comparing the nitration-products of anthragallol (Bamberger and Böck, Abstr., 1897, i, 596; 1902, i, 30) with those of its alkyl derivatives, the author has devised a suitable method of methylating anthragallol. *Anthragallol dimethyl ether*, $C_{14}H_5O_2(OMe)_2{\cdot}OH$, prepared by heating anthragallol, sodium carbonate, and excess of nitrobenzene at 150°, and then adding methyl sulphate, crystallises from alcohol in orange-coloured needles melting at 159—160°. The *sodium* and *lithium* derivatives are red. The *acetyl* derivative crystallises from alcohol in lemon-yellow needles which melt at 167°.

Anthragallol methyl ether, $C_{14}H_5O_2(OH)_2{\cdot}OMe$, prepared by heating the dimethyl ether with concentrated sulphuric acid at 100°, crystallises from alcohol in needles melting at 233° and forms a *diacetyl* derivative which crystallises in sulphur-yellow needles melting at 184°.

When the dimethyl ether is heated with concentrated sulphuric acid at 200°, the methyl groups are eliminated and anthragallol is formed.

The sodium derivative of the dimethyl ether does not react with methyl iodide, but when heated with methyl sulphate and sodium

carbonate at 180° yields *anthragallol trimethyl ether*, $C_{14}H_5O_2(OMe)_3$; this crystallises in citron-yellow needles and melts at 168°.

Perkin and Hummel (Trans., 1893, **63**, 1160) have described three anthragallol dimethyl ethers occurring in *Oldenlandia umbellata*, but none of those compounds is identical with the dimethyl ether examined by the author. A. McK.

The Occurrence of Nerol; a New Aliphatic Terpene Alcohol in Ethereal Oils. Hugo von Soden and Otto Zeitschel (*Ber.*, 1903, **36**, 265—267. Compare Hesse and Zeitschel, this vol., i, 189).—Nerol, to the extent of 15—20 per cent., may be readily obtained from American oil of petit-grain. The geraniol may be removed by aid of the compound, insoluble in light petroleum, which it forms with calcium chloride. *Neryl acetate*, obtained by the action of acetic anhydride on the alcohol, distils at 134° under 25 mm. pressure and has a sp. gr. 0·917 at 15°. The *formate* distils at 119—121° under 25 mm. pressure and has a sp. gr. 0·928 at 15°. J. J. S.

Lariciresinol. Hugo Hermann (*Monatsh.*, 1902, **23**, 1022—1031). —It has been shown by Bamberger and Landsiedl (Abstr., 1899, i, 929) that lariciresinol, from the resin of the larch tree, has the constitution $C_{17}H_{16}O_4(OMe)_2$, and contains four hydroxyl groups, of which two are phenolic and two alcoholic in character.

Diacetyl lariciresinol diethyl ether, $C_{17}H_{12}(OMe)_2(OEt)_2(OAc)_2$, prepared from lariciresinol diethyl ether, forms colourless needles and melts at 113°. *Anhydrolariciresinol*, $C_{17}H_{14}O_3(OMe)_2$, prepared by heating lariciresinol (the more fusible form melting at 104°) with alcoholic hydrogen chloride for several hours, forms a granular, crystalline mass and melts at 207°. Its *diacetyl* compound forms lustrous needles melting at 140°. *Anhydrolariciresinol dimethyl ether*, $C_{17}H_{12}O(OMe)_4$, prepared from anhydrolariciresinol by alkylation with methyl sulphate, forms spear-shaped crystals and melts at 148·5°. When lariciresinol, melting at 169°, is dissolved in concentrated aqueous solutions of hydrogen chloride or hydrogen iodide, it is converted into the isomeric form melting at 104—106°. Nitration of lariciresinol yields dinitroguaiacol, $OMe\cdot C_6H_2(NO_2)_2\cdot OH$. A. McK.

Preparation of Camphor from Pinene by the Action of Oxalic Acid. Iwan W. Schindelmeiser (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 954—959).—The action of oxalic acid on pinene yields an ester of inactive borneol, and not camphor, although a French patent has been taken out for the preparation of the latter substance in this way.

The best way of preparing borneol, and hence also camphor, is from the acetate of borneol, constituting 36—50 per cent. of the oil from the Siberian pine (*Abies sibirica*). T. H. P.

New Haloid Derivatives of Dextrorotatory Benzylidene- and Benzyl-camphor. Albin Haller and Jules Minguin (*Compt. rend.*, 1903, **136**, 69—73. Compare Abstr., 1901, i, 599).—In the

bromination of benzylcamphor (*loc. cit.*), two α-bromobenzylcamphors are obtained; one, melting at 91—92° and having $[\alpha]_D$ +20, which, when treated with alcoholic potash, yields ordinary benzylidenecamphor; the other, which melts at 94—95°, has $[\alpha]_D$ +61, and gives a benzylidenecamphor which resembles the ordinary compound in every respect except crystalline form. This fact was not observed in the previous investigation. The remainder of the paper gives an account of work which has been previously published (*loc. cit.*).

K. J. P. O.

Synthesis of a Bicyclic Bridged-ring System. PAUL RABE (*Ber.*, 1903, 36, 225—227).—The compound produced by the condensation of carvone and ethyl acetoacetate in presence of hydrogen chloride (Goldschmidt and Kisser, Abstr., 1887, 475, 923) has the formula $\begin{array}{l} CO_2Et\cdot CHAc\cdot \underset{|}{C}H\text{—}CH_2\cdot \underset{|}{C}H\cdot CMe_2Cl \\ \qquad\qquad\quad CHMe\cdot CO\cdot CH_2 \end{array}$; condensation with sodium ethoxide and elimination of the $-CO_2Et$ group does not yield the corresponding unsaturated compound $-CMe{:}CH_2$, but a keto-alcohol,

$$\begin{array}{lll} CH_2\cdot CH & \text{——} & CH_2 \\ CO \quad CHMe & & CH\cdot CMe{:}CH_2 \\ CH_2\cdot C(OH) & \cdot & CH \end{array} \quad \text{or} \quad \begin{array}{l} CH_2\cdot CH(CMe{:}CH_2)\diagdown \\ CH\cdot CH_2\cdot CMe(OH)\text{—}CH, \\ CHMe\text{—————}CO\diagup \end{array}$$

formed by internal condensation.

T. M. L.

Condensation of Ethyl Acetoacetate with Carvone in presence of Sodium Ethoxide. PAUL RABE and KARL WEILINGER (*Ber.*, 1903, 36, 227—233).—9-*Methyl*-3-iso*propenyl*dicyclo*nonane*-5-*ol*-7-*one*, $C_{13}H_{20}O_2$, the keto-alcohol formulated in the preceding abstract, boils at 182—183° under 12—15 mm. pressure, has a sp. gr. 1·0255 at 20°/4°, n_D 1·4992 at 20°, and $[\alpha]_D$ +18·8° at 15°; it is a colourless, viscid oil, miscible with most organic solvents, but not with water or light petroleum, and combines additively with 1 mol. of bromine, but not with phenylcarbimide. The *acetate* is an oil, boiling at 178—182° under 15 mm. pressure, and behaving as an unsaturated compound. Two stereoisomeric glycols are formed on reducing the ketone with sodium and alcohol. The solid *glycol*, $C_{13}H_{22}O_2$, crystallises from benzene in minute, rhombic leaflets, melts at 172—173°, has $[\alpha]_D$ −19·35° at 15° in alcohol, is not volatile with steam, but readily sublimes, and decolorises permanganate; the *dibromide*, $C_{13}H_{22}O_2Br_2$, crystallises from 40 per cent. alcohol in white flakes, and melts, becoming black and liberating gas, at 161°; the *diacetate* is an unsaturated oil and boils at 193—196° under 13 mm. pressure; the *monocarbanilide*, $C_{20}H_{27}O_3N$, sinters at 55—65°. The *liquid glycol* boils at 198° under 15 mm. pressure, has $[\alpha]_D$ = +11·75° at 15° in alcohol, decolorises permanganate, and forms a *dibromide*; the *diacetate* is an unsaturated oil and boils at 194—196° under 15 mm. pressure; the *monocarbanilide* sinters at 58° and melts with liberation of gas at 80°. The glycols do not combine with hydroxylamine.

T. M. L.

Condensation of Ethyl Acetoacetate with Carvone in presence of Hydrogen Chloride. PAUL RABE and KARL WEILINGER (*Ber.*, 1903, **36**, 234—238. Compare Abstr., 1887, 475; 1899, i, 289). —The *ketonic* "β"-form of ethyl chlorotetrahydrocarvonylaceto-acetate, formulated in a preceding abstract, melts at 146° and is converted by sodium ethoxide into the sodium salt of the *enolic* "α"-form, which was obtained as an oil, from which crystals of the ketonic ester were slowly deposited. Hydrolysis with aqueous-alcoholic potassium hydroxide yields eucarvone and the compound $C_{13}H_{20}O_2$. Heating with quinoline gave hydrogen chloride, ethyl acetoacetate, and carvacrol. T. M. L.

Action of Nitric Acid on Saturated Hydrocarbons and their Derivatives. VIII. Nitration of Dihydrocamphene and of Pinene Hydrochloride. MICHAËL I. KONOWALOFF and Z. KIKINE (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 935—944).—The action of dilute nitric acid on dihydrocamphene (camphane) yields a *nitro*-compound, $C_{10}H_{17}\cdot NO_2$, which separates from alcoholic solution in crystals melting at 125—129°; in benzene, it exhibits normal cryoscopic behaviour and has no action on polarised light; in the same solvent, it gives the molecular refraction (Lorenz and Lorentz formula) 48·60, the agreement of which with the calculated value 49·715 demonstrates the absence of a double linking in the compound; with the alkali hydroxides, it gives salts, the solutions of which yield, with ferric chloride and ether, the reaction for nitro-compounds, and with nitrous acid it gives the reaction only obtained with secondary nitro-compounds. Reduction of the nitro-derivative with zinc dust and acetic acid yields: (1) a small quantity of a *ketone* melting at 150—165° and giving an oxime melting at 58—64°: (2) an *amine*, $C_{10}H_{17}\cdot NH_2$, boiling in the impure condition between 194° and 204° and forming crystals which melt between the wide limits 65° and 130°; the *hydrochloride* and the *nitrate*, which melts at 210—215°, were prepared, and also the *platinichloride*, which consists of a mixture of two compounds of the composition $(C_{10}H_{17}\cdot NH_2)_2,H_2PtCl_6$, one blackening at 210° and the other at a much higher temperature; the *acetyl* derivative of the amine forms crystals melting within wide limits of temperature below 75° and two *benzoyl* derivatives are obtained which, when crystallised from benzene, melt at 133—139° and 70° respectively.

The action of bromine on a solution of the alkali salts of the nitro-compound yields a *bromonitro*-compound, $C_{10}H_{16}Br\cdot NO_2$, melting at 158—172°.

From these results, the author concludes that the nitro-compound obtained is not homogeneous but consists of a mixture of two isomeric compounds, one of which was obtained by Forster (Trans., 1897, **71**, 1030; 1899, **75**, 1141; 1900, **77**, 251) from camphoroxime, and gives two amines, bornylamine and neobornylamine (Trans., 1900, **77**, 1152).

The action of dilute nitric acid on pinene hydrochloride yields three compounds: (1) a primary *chloronitro*-derivative, $C_{10}H_{16}Cl\cdot NO_2$, not isolated in the pure state. (2) A secondary *chloronitro*-derivative, $C_{10}H_{16}Cl\cdot NO_2$, which separates from alcohol in crystals melting at 136—142°, and the molecular weight as determined cryoscopically in

benzene is normal; a 4·85 per cent. benzene solution in a 100 mm. tube rotates the plane of polarisation 1·26°; the action of bromine on the potassium compound yields a *chlorobromonitro*-compound melting at 105—110°. Reduction of the nitrochloro-compound with zinc dust and acetic acid gives the *chloroamine*, $C_{10}H_{16}Cl·NH_2$, which melts within wide limits and forms a *platinichloride* decomposing at 230°. (3) A tertiary *chloronitro*-derivative, $C_{10}H_{16}Cl·NO_2$, which separates from alcohol in crystals melting at 195—200° and, on reduction, yields a chloroamine, not investigated owing to its small quantity.

T. H. P.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1903, 36, 398—400. Compare Abstr., 1902, i, 482).—*Trimethylbrazilonoxime*, $C_{19}H_{18}O_5{:}NOH$, crystallises from acetic acid and melts at 203—205°; the *acetyl* derivative, $C_{21}H_{21}O_7N$, crystallises from alcohol in white flakes and melts at 179—182°.

Bromotrimethylbrazilin is oxidised by chromic acid to *bromotrimethylbrazilone*, $C_{19}H_{17}O_6Br$, which crystallises from acetic acid in needles, and becomes brown and melts at 225°. Acetic anhydride and sodium acetate convert it into *bromoacetyltrimethyldehydrobrazilin*, which crystallises from acetic acid in needles and melts at 271—274°.

Dinitrotetramethylhæmatoxylone, $C_{20}H_{20}O_{12}N_2$, crystallises from acetic acid in yellowish needles, and becomes brown and melts with liberation of gas at 187—192°.

T. M. L.

Catechin. ROBERT CLAUSER (*Ber.*, 1903, 36, 101—107. Compare Kostanecki and Tambor, Abstr., 1902, i, 553).—Air-dry catechin, melting at 96°, loses 15·4 per cent. of water in a vacuum and melts at 176°, but when dried at 100° it loses 20 per cent. of water and melts at 210°; these results are in accordance with the formulæ $C_{15}H_{14}O_6 + 4H_2O$, $+ 3H_2O$, and $+ H_2O$. The estimation of the acetyl groups in the acetyl derivative corresponded with the formula $C_{15}H_9O_6Ac$. Phloroglucinol is formed when catechin is hydrolysed by dilute alkali, even in the absence of air. By the action of ammonia, an OH group appears to be replaced by NH_2.

T. M. L.

Bromo*iso*pyromucic Acid. G. CHAVANNE (*Compt. rend.*, 1903, 136, 49—50).—*Bromo*iso*pyromucic acid*, $C_5H_3O_3Br$, obtained by the direct action of bromine on *iso*pyromucic acid (Abstr., 1901, i, 649), forms pale yellow crystals which melt at 172°. The *acetate*, $C_5H_2O_3BrAc$, and *benzoate*, $C_5H_2O_3BrBz$, melt at 76° and 123° respectively. The substitution of bromine has not modified the character of the enolic group of the original acid, for, with phenylhydrazine and hydroxylamine, it yields salts melting at 112° and 107—108° respectively, and not a hydrazone and oxime. The exact constitution of the acid is, however, still uncertain.

C. H. B.

New Class of Aromatic Compounds allied to Tetronic Acid. RICHARD ANSCHÜTZ (*Ber.*, 1903, 36, 463—466).—2 : 4-Dichlorosalicyl chloride, $OH·C_6H_2Cl_2·COCl$, readily reacts with ethyl sodiomalonate forming *ethyl* 6 : 8-*dichloro*-4-*hydroxycoumarin*-3-*carboxylate*,

$$C_6H_2Cl_2{<}{\substack{O—CO\\C(OH)}}{\gg}C·CO_2Et,$$

melting at 135°, which probably is the enolic form, since it decomposes sodium carbonate or ethyl sodiomalonate. When it is treated with aqueous alkali, 6:8-*dichloro-4-hydroxycoumarin*, $C_6H_2Cl_2<\begin{matrix}O-CO\\C(OH)\end{matrix}>CH$, is formed, which melts and decomposes at 284°.

The corresponding non-chlorinated derivatives can be prepared in a similar manner from acetylsalicyl chloride, which yields *ethyl 4-hydroxycoumarincarboxylate*, $C_6H_4<\begin{matrix}O-CO\\C(OH)\end{matrix}>C\cdot CO_2Et$, melting at 101°, and *4-hydroxycoumarin*, $C_6H_4<\begin{matrix}O-CO\\C(OH)\end{matrix}>CH$, melting at 206°. Both these substances are strongly acid, and when treated with aqueous ammonia yield ammonium salts. The silver salts are converted into the alkyl ethers by alkyl iodides. *4-Acetoxycoumarin*, $C_6H_4<\begin{matrix}O-CO\\C(OAc)\end{matrix}>CH$, melts at 103° and is decomposed by boiling water.

4-Hydroxycoumarin may be regarded as a phenylenetetronic acid, and like tetronic acid forms condensation products with aldehydes. *3-Methylenebis-4-hydroxycoumarin*, $CH_2\left(C<\begin{matrix}C(OH)\\CO-O\end{matrix}>C_6H_4\right)_2$, melts and decomposes at 260°; *3-ethylidenebis-4-hydroxycoumarin*,

$$CHMe\left(C<\begin{matrix}C(OH)\\O-CO\end{matrix}>C_6H_4\right)_2,$$

melts at 165°.

The *o*-substituted salicyl chlorides and the acetylsalicyl chlorides undergo similar reactions with ethyl sodiocyanoacetate and sodioacetoacetate, and 26 members of the 4-hydroxycoumarin class have already been prepared and will shortly be described. A. H.

Synthesis of Tetrone-α-carboxylic Ester and Tetronic Acid. RICHARD ANSCHÜTZ and W. BERTRAM (*Ber.*, 1903, 36, 468—472. Compare preceding abstract).—*Methyl tetrone-4-carboxylate*,

$$CH_2<\begin{matrix}C(OH)\\O\cdot CO\end{matrix}>C\cdot CO_2Me,$$

prepared by acting on methyl sodiomalonate with acetylglycollic chloride, boiling the resulting sodium compound with methyl alcohol, and then decomposing with hydrochloric acid, crystallises in small needles and melts and decomposes at 171—173° after becoming brown at 160°. The reaction may also be carried out in benzene solution, and the ester is then obtained directly by decomposing the sodium compound with hydrochloric acid. The *ammonium* derivative of methyl tetronecarboxylate, $CH_2<\begin{matrix}C(ONH_4)\\O-CO\end{matrix}>C\cdot CO_2Me$, is prepared by passing ammonia into a methyl-alcoholic solution of the ester, and crystallises in very slender, silky needles, which become brown at 180° and melt and blacken at 200—205°; the *methylammonium* derivative crystallises in flat plates and melts and decomposes at 177—178°.

Ethyl tetrone-4-carboxylate, prepared from ethyl sodiomalonate, crystallises in needles melting at 124—125°. When methyl tetronecarboxylate is heated with a solution of sodium methoxide in dilute

methyl alcohol, sodium tetronate is produced, from which pure tetronic acid can be isolated. A. H.

Condensation Product formed from Methylacetylacetone and *m*-Dihydroxybenzene. CARL BÜLOW (*Ber.*, 1903, 36, 190—194. Compare Abstr., 1901, i, 400, 559, and 603; and 1902, i, 112, 113, and 484).—When hydrogen chloride is passed into a solution of resorcinol and methylacetylacetone in acetic acid containing a few drops of acetic anhydride, the liquid becomes intensely yellow, and the *hydrochloride* of *anhydro-7-hydroxy-2 : 3 : 4-trimethyl-1 : 4-benzopyranol*, $\begin{matrix} OH\cdot C{=\!=}CH\cdot C\cdot O(HCl)\cdot CMe \\ CH{:}CH\cdot C\cdot C({:}CH_2)\cdot CMe \end{matrix}$, separates; it crystallises from a mixture of alcohol and hydrochloric acid in lemon-yellow needles with H_2O. On adding sodium acetate to a solution of the hydrochloride, the free *base* separates in orange-coloured flakes. The *picrate*, prepared by adding an alcoholic solution of picric acid to the acetic acid solution of the hydrochloride, forms lustrous crystals. The *platinichloride* forms brown needles and the *aurichloride* a pale yellow, crystalline precipitate.

Resorcinol and ethyl benzoylacetoacetate yield, not a benzopyranol derivative, but β-phenylumbelliferone (compare von Pechmann and Hanke, Abstr., 1901, i, 210). K. J. P. O.

Synthesis of 7:8-Dihydroxychromone. ELKAN DAVID and STANISLAUS VON KOSTANECKI (*Ber.*, 1903, 36, 125—129).—Gallacetophenone dimethyl ether, which is best prepared by the action of methyl sulphate on gallacetophenone, readily reacts with ethyl oxalate in presence of metallic sodium to form a ketonic ester, which is probably ethyl 2-hydroxy-3 : 4-dimethoxybenzoylpyruvate,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et.$$

The crude product, when boiled with hydrochloric acid, yields 7 : 8-*dimethoxychromone-2-carboxylic acid*,

$$\begin{matrix} OMe\cdot C{:}C(OMe)\cdot C{-}O{-}C\cdot CO_2H \\ CH{:}CH{-\!-}C\cdot CO\cdot CH \end{matrix},$$

which crystallises in needles melting and losing carbon dioxide at 272°. When this substance is heated above its melting point, 7 : 8-*dimethoxychromone* is formed, which crystallises, with H_2O, in long needles. The anhydrous substance melts at 124° and forms a faintly yellow, non-fluorescent solution in sulphuric acid. 7 : 8-*Dihydroxychromone*, $C_6H_2(OH)_2{<}\begin{matrix} O{-\!-}CH \\ CO\cdot CH \end{matrix}$, obtained by the action of hydriodic acid on the methyl ether, crystallises, with $2H_2O$, in long, lustrous needles. The anhydrous substance melts at 262° and gives the catechol reaction with ferric chloride. The *diacetyl* compound,

$$C_9H_4O_2(OAc)_2,$$

forms long plates melting at 110°. A. H.

Cyclic Compounds containing Sulphur. WILHELM AUTENRIETH and A. BRÜNING (*Ber.*, 1903, 36. 183—190. Compare Abstr., 1901, i, 560; and 1902, i, 389).—*cycloDithiodi*-o-*xylylene*,

$$C_6H_4{<}\begin{matrix} CH_2\cdot S\cdot CH_2 \\ CH_2\cdot S\cdot CH_2 \end{matrix}{>}C_6H_4,$$

is prepared by boiling *o*-xylylene bromide and *o*-xylylene mercaptan in mol. proportion with alcoholic sodium ethoxide: the product, which is difficult to purify, crystallises in slender, colourless needles melting at 234—236°. When treated with bromine in chloroform solution, it is converted into a dibromide, $C_6H_4<\begin{matrix}CH_2\cdot SBr\cdot CH_2\\ CH_2\cdot SBr\cdot CH_2\end{matrix}>C_6H_4$, which crystallises in needles melting at 110—112°, and does not lose bromine when boiled with aqueous sodium hydroxide or shaken with cold moist silver oxide, but only when heated with the latter. cyclo*Di-o-xylylenedisulphone*, $C_6H_4<\begin{matrix}CH_2\cdot SO_2\cdot CH_2\\ CH_2\cdot SO_2\cdot CH_2\end{matrix}>C_6H_4$, is prepared by shaking a benzene solution of the thio-compound with acidified aqueous potassium permanganate; it crystallises from alcohol in sparingly soluble plates melting above 320°, and is stable towards alkali hydroxides.

o-*Xylylenemonosulphone*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>SO_2$, the first cyclic monosulphone, is obtained by oxidising *o*-xylylene sulphide, prepared by Leser's method (Abstr., 1884, 1313), with acidified permanganate; it is very stable and crystallises in long prisms melting at 150—152°.

K. J. P. O.

Condensation Products of Rhodanic Acid and Allied Substances with Aldehydes. ARTHUR ZIPSER (*Monatsh.*, 1902, 23, 958—972).—It has been shown that benzaldehyde condenses with rhodanic acid to form benzylidenerhodanic acid (Nencki and Bourquin, Abstr., 1885, 40), whilst *o*- and *p*-nitrobenzaldehydes yield the corresponding nitrobenzylidenerhodanic acids (Bondzýnski, Abstr., 1887, 1109).

o-*Hydroxybenzylidenerhodanic acid*, $OH\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NH\\ S-CS\end{matrix}$, prepared by condensing salicylaldehyde and rhodanic acid, melts at 200° with decomposition. It is readily soluble in alkalis and is reprecipitated by acids. Its mono*acetyl* derivative crystallises from alcohol in golden-yellow needles melting at 168°.

o-*Hydroxybenzylidenethiohydantoin*, $HO\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NH\\ S-C:NH\end{matrix}$, prepared from salicylaldehyde and thiohydantoin, melts at 215° with decomposition. Its mono*acetyl* derivative crystallises from alcohol in needles which melt indistinctly and decompose at 223—228°.

o-*Hydroxybenzylidenedioxythiazole*, $HO\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NH\\ S-CO\end{matrix}$, from salicylaldehyde and dioxythiazole, crystallises from alcohol in yellow needles melting at 230°. It may also be prepared by boiling *o*-hydroxybenzylidenethiohydantoin with strong hydrochloric acid. Its mono*acetyl* derivative melts at 171°.

Cinnamylidenerhodanic acid, $CHPh:CH\cdot CH:C<\begin{matrix}CO\cdot NH\\ S-CS\end{matrix}$, prepared in similar manner, melts indistinctly and decomposes at 208—211°. When it is heated with baryta, thiocyanic acid and *a-thiolcinn-*

amenylacrylic acid, CHPh:CH·CH:C(SH)·CO_2H, are formed. The latter forms microscopic needles, melts at 149°, and is insoluble in water, but soluble in acetone, ether, or benzene; its alkaline solution gives a characteristic dirty, emerald-green coloration with ferric chloride. Its *benzyl* derivative, CHPh:CH·CH:C(S·C_7H_7)CO_2H, melts at 164°. *Cinnamylidenethiohydantoin*, $\mathrm{CHPh{:}CH{\cdot}CH{:}C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{S{-}{-}C{:}NH}\end{matrix}$, crystallises in needles which blacken at 235°, and *cinnamylidenedioxythiazole*, $\mathrm{CHPh{:}CH{\cdot}CH{:}C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{S{-}{-}CO}\end{matrix}$, melts at 214—216°.

The acetyl derivatives described differed from their parent substances in not having dyeing properties. A. McK.

Decomposition of Yohimbine by means of Alkali Hydroxides. LEOPOLD SPIEGEL (*Ber.*, 1903, 36, 169—171).—When yohimbine is boiled with concentrated alcoholic potassium hydroxide, it is converted into a substance which is the potassium salt of a new alkaloid, *noryohimbine*, $C_{20}H_{26}O_4N_2$. From the salt, this compound can be obtained by treatment with acetic acid; it crystallises from water in lustrous prisms melting and decomposing at 257—260°, and is soluble both in alkalis and acids; it does not appear to be a phenol, but a true carboxylic acid; attempts to reconvert it into yohimbine, either by the action of methyl iodide and an alkali hydroxide or by esterification, were fruitless. Owing to the composition of this substance, it is probable that yohimbine has the formula $C_{21}H_{28}O_4N_2$ instead of $C_{22}H_{30}O_4N_2$.

K. J. P. O.

Action of Sulphuryl Chloride and of Bromine on Pyrrole. III. GIROLAMO MAZZARA (*Gazzetta*, 1902, 32, ii, 313—319. Compare Abstr., 1902, i, 820; this vol., i, 51).—*Chlorotribromopyrrole*, C_4NHBr_3Cl, obtained by the successive action of sulphuryl chloride (2 mols.) and bromine (2 mols.) on an ethereal solution of pyrrole, separates from light petroleum in large prismatic crystals which appear rose-red by transmitted light, but in mass have the colour of cobaltous salts; it has the normal molecular weight as shown by cryoscopic determinations in benzene, and just above 100° decomposes with evolution of gas.

Dichlorodibromopyrrole, $C_4NHBr_2Cl_2$, obtained by the interaction, in ethereal solution, of pyrrole, sulphuryl chloride (3 mols.), and bromine (1 mol.), crystallises from light petroleum in large, shining scales; in benzene, it exhibits normal cryoscopic behaviour, and when heated to 100—113° it decomposes.

It will be observed that the amounts of bromine used in the above preparations are less than those required by theory, whilst the sulphuryl chloride is used in excess. T. H. P.

Ethyl *N*-Dimethyldicarboxypyrryl-*p*-benzoylpyruvate. CARL BÜLOW and ERNST NOTTBOHM (*Ber.*, 1903, 36, 392—397).—*p*-Aminoacetophenone, when boiled with ethyl diacetylsuccinnate and acetic acid, yields *ethyl N-2 : 5-dimethyl-3 : 4-dicarboxypyrryl-*p*-acetophenone*,

$$\begin{matrix}\mathrm{CO_2Et{\cdot}C{:}CMe}\\ \mathrm{CO_2Et{\cdot}C{:}CMe}\end{matrix}>\mathrm{N{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3},$$

which crystallises from acetic acid in glistening, colourless needles, melts at 114°, and is soluble in organic solvents. Unlike the *p*-aminoacetophenone, which yields only an *N*-acetyl derivative with ethyl acetate and sodium ethoxide, the tertiary base condenses with ethyl oxalate to form the *diketone*,

$$\begin{matrix} CO_2Et\cdot C\text{:}CMe \\ | \\ CO_2Et\cdot C\text{:}CMe \end{matrix} > N\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et,$$

which crystallises from dilute acetone in well-defined, yellow, glistening crystals, melts at 123°, forms a grey-green copper salt soluble in chloroform, dissolves in cold aqueous sodium hydroxide, and is reprecipitated unchanged by carbon dioxide; when the ester is boiled with more concentrated alkalis, the $-CO\cdot CO_2Et$ group is again eliminated. The *benzeneazo*-derivative of the diketone, $C_{30}H_{31}O_8N_3$, crystallises from dilute alcohol in yellow needles and melts at 122°. Hydroxylamine converts the diketone into the iso*oxazole*,

$$\begin{matrix} CO_2Et\cdot C\text{:}CMe \\ | \\ CO_2Et\cdot C\text{:}CMe \end{matrix} > N\cdot C_6H_4\cdot C < \begin{matrix} N-O \\ \quad\ | \\ CH\text{:}C\cdot CO_2Et, \end{matrix}$$

which crystallises from alcohol in colourless needles and melts at 189°. The *semicarbazone*, $C_{25}H_{30}O_8N_4$, crystallises from dilute acetic acid, melts at 134°, and is readily soluble in organic solvents. T. M. L.

By-product in the Preparation of Stilbazole. ALBERT LADENBURG (*Ber.*, 1903, 35, 118—119).—A *base*, $C_{20}H_{17}N$, which is probably diphenylpyridyltrimethylene, $\begin{matrix} CHPh \\ | \\ CHPh \end{matrix} > CH\cdot C_5NH_4$, is produced as a by-product in the preparation of α-stilbazole from benzaldehyde, α-picoline, and zinc chloride; it is much less soluble in alcohol than the stilbazole, but crystallises from benzene in snow-white forms melting at 164°, which have a pale violet fluorescence. The *hydrochloride*,

$$C_{20}H_{17}N,HCl,$$

crystallises from hot alcohol in needles. The *sulphate*, *mercurichloride*, *aurichloride*, and *platinichloride* were also prepared. The *dinitro*-derivative, $C_{20}H_{15}N(NO_2)_2$, melts at 112°. T. M. L.

Derivatives of α-Stilbazole. ALBERT LADENBURG and EMANUEL KROENER (*Ber.*, 1903, 36, 119—125).—*α-Phenyl-β-pyridylethyleneglycol*, $OH\cdot CHPh\cdot CH(C_5NH_4)\cdot OH$, prepared from stilbazole dibromide and silver oxide, crystallises from hot water in pearly scales and melts at 144—145°. The *hydrochloride*, $C_{13}H_{13}O_2N,HCl,2H_2O$, crystallises in minute needles and melts at 186—187°. The *platinichloride*, $(C_{13}H_{13}O_2N)_2,H_2PtCl_6$, forms minute, reddish crystals, dissolves readily in water and alcohol, and melts at 156—157°. The *picrate*, $C_{13}H_{13}O_2N,C_6H_2(NO_2)_3OH$, crystallises from alcohol in minute needles, and melts at 171—172°. The *diacetyl* derivative crystallises from alcohol in snow-white needles and melts at 36—37°. The *dibenzoyl* derivative crystallises from alcohol in white needles and melts at 88—89°; its hydrochloride crystallises from dilute alcohol with H_2O and melts at 119—120°.

α-Phenyl-β-pyridylvinyl alcohol, $C_{13}H_{11}ON$, prepared by heating the dibromide at 115—125° with alcoholic potassium hydroxide, crystallises

from ether in yellow needles and melts at 50—51°; the *hydrochloride*, $C_{13}H_{11}ON,HCl,2H_2O$, crystallises in snow-white, silky needles and begins to sublime at 95—100°. The *platinichloride*,

$$(C_{13}H_{11}ON)_2,H_2PtCl_6,$$

crystallises from alcoholic hydrogen chloride and melts at 163—164°. The *picrate* crystallises from alcohol in beautiful, yellow flakes and melts at 176—177°. The base does not interact with hydroxylamine or phenylhydrazine, and appears to be entirely enolic. The *benzoate* crystallises from a mixture of ether and alcohol in compact prisms and melts at 90—91°; its *hydrochloride* crystallises in transparent needles and melts at 128—129°, and the *picrate* crystallises from alcohol in rhombic tablets and melts and decomposes at 175—176°.

α-Phenyl-β-pyridylethanedione, $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_5NH_4$, prepared by the action of nitric acid on the glycol, melts at 78—79°. The *hydrochloride* crystallises in transparent, glassy prisms and melts at 124—125°. The *picrate* crystallises in needles and melts at 87—88°.

T. M. L.

Physico-chemical Investigations in the Pyridine Series. EMIL J. CONSTAM and JOHN WHITE (*Amer. Chem. J.*, 1903, **29**, 1—49). —The carefully purified bases used in the experiments described in this paper had the following constants. Pyridine and α-, β-, and γ-picolines boiled at 115·2°, 128·8°, 143·4°, and 143·1° respectively under 760 mm. pressure, and had the sp. gr. 0·989305, 0·94972, 0·96134, and 0·95714 at 15°/4°.

The heats of combustion of pyridine and α-, β-, and γ-picolines are 658·8, 815·4, 812·4, and 816·0 Cal. at constant volume, and 659·2 816·1, 813·1, and 816·7 Cal. at constant pressure at 15° respectively; their heats of formation are −16·7, −10·6, −7·6, and −11·2 Cal. These figures show that there is a constant difference between the heats of combustion of pyridine and its higher homologues which has a mean value of about 156 Cal., corresponding with a difference in composition of CH_2; the same value has been found by other observers, particularly Stohmann (Abstr., 1887, 428), for homologous compounds of both the aliphatic and aromatic series. A single determination of the heat of combustion of lutidine gave 967·9 Cal. at constant volume and 968·9 Cal. at constant pressure. From these results, the following formula is established for the approximate calculation of the heats of combustion of the pyridine compounds from their empirical formulæ: $C_nH_{2n-5}N = 659{\cdot}2$ Cal. $+ (n-5)$ 156 Cal. The heats of formation may be calculated from the formula $C_nH_{2n-5}N = -51{\cdot}7$ Cal. $+ (n \times 7)$ Cal. On comparing the heats of combustion of the picolines with that of the metameric compound, aniline, determined by Petit (Abstr., 1888, 773), it is seen that the rule which has been established for the aliphatic and aromatic series is also valid for the pyridine compounds, namely, that isomerides possess practically the same heats of combustion, whilst metameric compounds have a higher value.

The specific heats of pyridine and α- and β-picolines were determined. The results show that between the same range of temperatures the

specific heats of α- and β-picolines are practically identical, and that their true specific heat may be calculated from the equation $C_t = 0{\cdot}3848 + 0{\cdot}000774t$; for pyridine, the equation is $C_t = 0{\cdot}3915 + 0{\cdot}000484t$.

The heats of evaporation of pyridine, α-picoline, and β-picolines are 107·33, 92·7, and 94·82 Cal. respectively; the values for the Trouton constant, $MH/T = C$, are 21·9, 21·5 and 21·3, and it is therefore evident that in the pyridine series the molecular heats are proportional to the absolute temperatures at which evaporation takes place. The constant expressing the molecular rise in the boiling point obtained by inserting the normal heats of evaporation in the formula, $K = 0{\cdot}02T/H$, gives for pyridine K 28·4, for α-picoline K 34·6, and for β-picoline K 35·8.

The heats of neutralisation were determined with $N/2$ hydrochloric acid and an $N/2$ solution of the base; the values found were, for pyridine, 4776·2, for α-picoline, 5979·6, and for β-picoline, 5689·8 Cal.; it is seen that both picolines have a heat of neutralisation higher than that of pyridine, α-picoline giving a somewhat higher value than the β-compound. It is shown later that the affinity constants follow the same order.

The conductivities of picric acid and of its sodium salt were determined at dilutions varying from $v = 32$ to $v = 1024$; for picric acid, $\mu\infty = 356$, and for sodium picrate $\mu\infty = 74{\cdot}1$; hence the velocity of the picric ion is found to be 26·0. The conductivities of the picrates of the pyridine bases gave for $\mu\infty$ the following values: pyridine, 72·4; α-picoline, 66·8; β-picoline, 68·4; γ-picoline, 66·3; hence the velocities of the respective cathions are 46·4, 40·8, 42·8, and 40·3. By adding the value, 174, given by Kohlrausch for the OH ion at infinite dilution to the velocities of the ions of the bases, the following values are obtained for the conductivity of the hydrates of the bases at infinite dilution: pyridine hydrate, 230·1; α-picoline hydrate, 224·5; β-picoline hydrate, 226·5; γ-picoline hydrate, 224·0. The values found for the cathions of the picolines show that the cathions of the pyridine series conform to the rule that "isomeric ions have the same velocity of transport." Attention is drawn to the fact that the β-compound has a value slightly different from the others, which is in accord with the variation found in the heats of combustion.

The affinity constants were determined by Walker's method (Abstr., 1890, 5) with the following results: pyridine, $3{\cdot}0 \times 10^{-9}$; α-picoline, $3{\cdot}2 \times 10^{-8}$; β-picoline, $1{\cdot}1 \times 10^{-8}$; γ-picoline, $1{\cdot}1 \times 10^{-8}$.

From determinations of the refractive indices, the following molecular refractions were obtained: for pyridine, 23·94; α-picoline, 28·95; β-picoline, 28·83. These values agree closely with those found by Brühl (Abstr., 1895, ii, 194). The molecular refraction of γ-picoline is 28·92. E. G.

Aminopyridinecarboxylic Acids. Hans Meyer (*Monatsh.*, 1902, **23**, 942—946).—The author has previously shown (Abstr., 1901, i, 190) that 2-aminopyridine-5-carboxylic and 6-aminopyridine-5-carboxylic acids require, respectively, one equivalent of potassium hydroxide solu-

tion for neutralisation, but it was thought possible that the amount of alkali might vary according to the position of the amino-substituent relatively to the nitrogen. It is now shown that such is the case with 4-aminopyridine-5-carboxylic and 2 : 6-dimethyl-4-aminopyridine-3 : 5-dicarboxylic acids, which require for their neutralisation only a portion of the calculated amount of alkali. Since the necessary quantity of alkali increases with rise of temperature, those acids are regarded as having a betaine structure. When 2 : 6-dimethyl-4-aminopyridine-3 : 5-dicarboxylic acid is titrated against standard alkali at laboratory temperature, it behaves like a monobasic acid (compare Marckwald, Abstr., 1894, i, 381). The comportment of 5-aminopyridine-4-carboxylic acid towards standard alkali was normal. A. McK.

Indole Dyes. MARTIN FREUND and GUSTAV LEBACH (*Ber.*, 1903, 36, 308—309).—It was found by Fischer (Abstr., 1888, 283) that methylketole (2-methylindole, 2 mols.) condensed with aldehydes (1 mol.) with elimination of water to form leuco-bases which yield dyes of the rosaniline type, and probably have the formula $CHR\left(C{<}{C_6H_4 \atop CMe}{>}NH\right)_2$. 2-Methylindole and aldehydes also condense in mol. proportions, producing leuco-bases, probably represented by the expression $CHR\colon C{<}{C_6H_4 \atop CMe}{>}N$.

The following compounds have been prepared; (1) by interaction of 1 mol. of an aldehyde and 2 mols. of 2-methylindole; from *o*-nitrobenzaldehyde, pale yellow needles melting at 244°; from *p*-nitrobenzaldehyde, pale yellow prisms or scales melting at 238°; from *o*-chlorobenzaldehyde, colourless needles melting at 240°; from *m*-hydroxybenzaldehyde, pale yellow crystals melting at 222°; from *o*-chloro-*p*-dimethylaminobenzaldehyde, snow-white needles melting at 236°; from *p*-dimethylaminobenzaldehyde, snow-white prisms or needles melting at 226°; (2) by interaction of mol. proportions of the aldehyde and methylindole; substances were prepared from each of the aldehydes just mentioned; the *hydrochloride* of the base from *o*-nitrobenzaldehyde forms pale brown leaflets; the *base* from *p*-nitrobenzaldehyde is a crystalline, yellowish-brown substance; the *hydrochloride* from *o*-chlorobenzaldehyde forms pale yellow, lustrous scales melting at 194—195°; the *hydrochloride* from *m*-hydroxybenzaldehyde crystallises in yellowish-brown scales melting at 222°, the *base* from *o*-chloro-*p*-dimethylaminobenzaldehyde in yellowish-brown crystals melting at 282°; from *p*-dimethylaminobenzaldehyde, an amorphous base is obtained. K. J. P. O.

Ammonium Compounds. HERMANN DECKER (*Ber.*, 1903, 36, 261).—8-*Nitroquinoline methiodide*, prepared from 8-nitroquinoline by combination with ethyl sulphate and subsequent action of methyl iodide, is an orange-coloured, crystalline compound which loses its methyl iodide completely at 150—160°; the compound is of interest as showing that a nitro-group in the ortho-position does not entirely prevent the formation of a methiodide. T. M. L.

6-Alkyloxy- and 6-Hydroxy-quinolones. JOH. HOWITZ and M. BÄRLOCHER (*Ber.*, 1903, 36, 456—462. Compare *J. pr. Chem.*, 1892, ii, 46, 117).—The hydroxides resulting from the decomposition of the alkyl halogen additive compounds of the 6-hydroxyquinolines contain the hydroxyl group united with nitrogen, and hence do not yield quinolones on oxidation. The corresponding alkyloxyquinolines, however, readily yield quinolones, and from these the 6-hydroxyquinolones can be obtained by hydrolysis. 6-*Methoxy*-1-*methylquinolone*,

$$\begin{array}{l} \quad\;\; CH{:}CH\cdot C\cdot NMe{:}CO \\ OMe\cdot C{:}CH{-}C\cdot CH{=}CH \end{array},$$

is prepared by the oxidation of 6-methoxyquinoline methiodide with alkaline potassium ferricyanide, and crystallises in slender needles melting at 75°. 6-*Ethoxy*-1-*ethylquinolone* forms small, slender needles melting at 84°. 6-*Hydroxy*-1-*methylquinolone* is obtained by heating the methoxy-compound with hydrochloric acid at 180—200°, and crystallises in prisms melting at 218—220°. 6-*Hydroxy*-1-*ethylquinolone* forms lustrous needles or scales melting at 208—210°. 5-*Bromo*-6-*methoxyquinoline* is obtained by the methylation of the corresponding hydroxy-compound, and forms slender, yellowish-white needles or broad crystals melting at 94—95°. 5-*Bromo*-6-*ethoxyquinoline* has previously been described by Vis (Abstr., 1893, i, 606). 5-*Bromo*-6-*methoxyquinoline methiodide* forms yellow needles, which are sparingly soluble in water and melt and decompose at 220°. 5-*Bromo*-6-*ethoxyquinoline methiodide* crystallises in yellow needles and melts and decomposes at 215°. 5-*Bromo*-6-*ethoxyquinoline ethobromide* crystallises with $3H_2O$ in small tablets; the anhydrous compound melts at 195°. 5-*Bromo*-6-*methoxy*-1-*methylquinolone* crystallises in slender, yellowish-white needles or small, compact prisms melting at 168—170°. 5-*Bromo*-6-*ethoxy*-1-*methylquinolone* forms lustrous needles melting at 136—137°. 5-*Bromo*-6-*ethoxy*-1-*ethylquinolone* forms matted, colourless needles melting at 95—97°. Both 5-bromo-6-methoxy-1-methylquinolone and 5-bromo-6-ethoxy-1-methylquinolone are hydrolysed by hydrochloric acid to 5-*chloro*-6-*hydroxy*-1-*methylquinolone*, the bromine atom being replaced by chlorine. The product crystallises in yellowish-white needles or prisms which melt and decompose at 290°.

A. H.

Nitro-derivatives of Phenoxazine and the Analogue of Lauth's Violet in the Oxazine Series. FRIEDRICH KEHRMANN and A. SAAGER (*Ber.*, 1903, 36, 475—484).—The simplest oxazine colouring matter, $\begin{array}{l} \qquad\quad CH{:}CH\cdot C{=}N{-}C\cdot CH{:}CH \\ NH_2\cdot C{=}CH\cdot C{:}OCl\cdot C\cdot CH{:}C\cdot NH_2 \end{array}$, has not previously been prepared, although Bernthsen (Abstr., 1887, 665) showed that a colouring matter is obtained by nitrating phenoxazine and reducing and oxidising the resulting leuco-base. The necessary dinitrophenoxazine is best prepared from 6-*acetylphenoxazine*, $C_6H_4<\substack{NAc \\ O}>C_6H_4$, which crystallises in colourless prisms melting at 142°. On nitration in presence of glacial acetic acid at 0°, a small amount of a tetranitro-compound, sparingly soluble in benzene, is formed, together with

6-*acetyl*-3 : 9-*dinitrophenoxazine*, $NO_2\cdot C_6H_3<\overset{NAc}{\underset{O}{}}>C_6H_3\cdot NO_2$, which is readily soluble in benzene, crystallises in light brownish-yellow needles, and melts at 192°. 3 : 9-*Dinitrophenoxazine*, prepared from the acetyl derivative, crystallises in dark red, hair-like needles, which have a green lustre and decompose slowly above 200°. It forms a green solution in sulphuric acid and yields a *sodium* compound, crystallising in glittering, golden needles, which are decomposed by water. 3 : 9-*Diaminophenoxazine* is obtained as the *double* salt with stannic chloride by the reduction of the nitro-compound with stannous chloride and hydrochloric acid. This salt crystallises in colourless needles and is rapidly oxidised by air in aqueous solution. The hydrochloride of the base changes, on oxidation, into 3 : 9-*diaminophenoxazonium chloride*, $NH_2\cdot C_6H_3\ll\overset{N}{\underset{OCl}{}}>C_6H_3\cdot NH_2+H_2O$, which crystallises in matted needles, sometimes bronze, sometimes metallic green, in colour. It forms reddish-violet, strongly fluorescent solutions in both alcohol and water, and dyes cotton violet-blue on tannic acid, the shade being redder than that produced by Lauth's violet. Aqueous sodium hydroxide precipitates the brown, flocculent base, whilst sodium nitrite yields a yellowish-red diazo-compound which, when boiled with alcohol, is converted into a yellowish-red, fluorescent colouring matter. This is probably a monaminophenazoxonium compound, and is converted by aniline into a blue colouring matter. The chloride bears the same relation to the phenoxazine colouring matters (Capri-blue series) as does Lauth's violet to the methylene-blue colouring matters. The *dichromate*, $(C_{12}H_{10}ON_3)_2Cr_2O_7$, crystallises in needles with a bronze lustre, the *platinichloride* in small, metallic green needles, the *nitrate* in small, bronze-coloured needles.

3 : 5 : 7 : 9-*Tetranitrophenoxazine*, $C_{12}ONH_5(NO_2)_4$, is formed in small amount by the nitration of acetylphenoxazine and also by the nitration of 3 : 5-dinitrophenoxazine (Turpin, Trans., 1891, **59**, 714) and of 5 : 7-dinitrophenoxazine, and crystallises in plates or needles which show no definite melting point, but decompose gradually above 210°. The *sodium* salt crystallises in long, green needles, and is decomposed by a large amount of water. The corresponding 3 : 5 : 7 : 9-*tetra-aminophenazoxonium chloride*,

$$C_6H_2(NH_2)_2\ll\overset{N}{\underset{OCl}{}}>C_6H_2(NH_2)_2,$$

is a metallic green powder which forms a violet, non-fluorescent aqueous solution. 3 : 5 : 9-*Trinitrophenoxazine*, $C_{12}ONH_6(NO_2)_3$, is also formed by the nitration of 3 : 5-dinitrophenoxazine and crystallises either in metallic green spangles or with 1 mol. of acetic acid in lustrous, concentric needles. The corresponding *triaminophenoxazine hydrochloride* crystallises in colourless needles, and by oxidation is converted into the corresponding 3 : 5 : 9-*triaminophenoxazonium chloride*, which is a greenish-black powder and forms a magenta-coloured, non-fluorescent solution in water. The *dichromate* is an almost insoluble, brown, flocculent precipitate.

The constitution of the new dinitrophenoxazine is based on the analogy of the colouring matter obtained from it with Lauth's violet.

The constitution of this being known, the positions of three groups in the tetranitro-derivative are known, but that of the fourth is still uncertain. A. H.

Condensation of Aromatic *m*-Diamines with Chloroform to form Colouring Matters. ARTHUR WEINSCHENK (*Chem. Zeit.*, 1903, 27, 13).—When *m*-phenylenediamine is heated with excess of chloroform at 190—200° for several hours under pressure, and the product, after the evaporation of the chloroform, extracted with hydrochloric acid, a solution is obtained, from which sodium chloride throws down a brown dye capable of dyeing cotton in the absence of a mordant. *m*-Tolylenediamine gives a similar dye. K. J. P. O.

Substitution Derivatives of Diacylated Benzenoid Diamines with Different Acid Radicles. I. G. KOLLER (*Ber.*, 1903, 36, 410—417).—m-*Acetylaminophenyloxamic acid*,

$$NHAc\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2H,$$

obtained by acetylating *m*-aminophenyloxamic acid by Pinnow's method (Abstr., 1900, i, 214), crystallises from water in slender, colourless needles and melts and decomposes at 209° (Schiff and Ostrogovich, Abstr., 1897, i, 144, describe a substance of this name as melting at 125°).

p-*Aminophenyloxamic acid*, $NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2H$, obtained by boiling *p*-phenylenediamine with a hot concentrated solution of oxalic acid, crystallises from alcohol in colourless needles and darkens at 250°, but does not melt at 280°; it gives a *barium* salt crystallising in white needles, and an *acetyl* derivative, $NHAc\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2H$, which forms colourless needles and darkens at 240° without melting.

Ethyl p-*acetylaminophenyloxamate*, prepared by boiling *p*-aminoacetanilide with ethyl oxalate in alcoholic solution, crystallises from dilute alcohol, and melts and decomposes at 193°.

On nitration in concentrated sulphuric acid solution with potassium nitrate at $-10°$ to $-5°$, *p*-acetylaminophenyloxamic acid gives a *mononitro*-derivative of the constitution [$NHAc : NO_2 : NH = 1 : 3 : 4$]; it crystallises from dilute acetic acid in reddish-yellow needles, melts and decomposes at 228°, and on partial hydrolysis, best with aqueous ammonia at the ordinary temperature, yields 3-nitro-4-aminoacetanilide (Bülow and Mann, Abstr., 1897, i, 339).

When, however, the nitration is effected in fuming nitric acid of sp. gr. 1·5 at the same temperature, the principal product is m-*nitro*-p-*acetylaminophenyloxamic acid* [$NHAc : NO_2 : NH = 1 : 2 : 4$], which crystallises from alcohol in bright yellow needles, melts at 209°, and on partial hydrolysis with ammonia gives m-*nitro*-p-*aminophenyloxamic acid*; the latter crystallises from water, melts at 215°, and is easily convertible, by the diazo-reaction, into *m*-nitroaniline.

Ethyl o-*nitro*-p-*acetylaminophenyloxamate*,

$$NHAc\cdot C_6H_3(NO_2)\cdot NH\cdot CO\cdot CO_2Et,$$

obtained by nitrating ethyl *p*-acetylaminophenyloxamate in sulphuric acid solution, crystallises from dilute alcohol in slender, yellow needles and melts at 174°. The isomeric *ethyl* m-*nitro*-p-*acetylaminophenyloxamate*, obtained on nitration in fuming nitric acid, forms reddish-

yellow needles and melts at 179°. On partial hydrolysis, these esters give the same products as the parent acids. W. A. D.

Hydroxyamidines. HEINRICH LEY and E. HOLZWEISSIG (*Ber.*, 1903, 36, 18—24).—The hydroxyamidines obtained according to the two equations: I, $CRCl{:}NR^{1} + NHR^{11}{\cdot}OH = HCl + NR^{1}{:}CR{\cdot}NR^{11}{\cdot}OH$, and II, $CRCl{:}NR^{11} + NHR^{1}{\cdot}OH = HCl + NR^{11}{:}CR^{1}{\cdot}NR^{1}{\cdot}OH$, are different, not identical; the contrast between the immovability of the hydroxyl group in these compounds and the mobility of the hydrogen atom in the amidines is striking.

Benzylbenzimide chloride, $CPhCl{:}NBz$, obtained by the interaction of phosphorus pentachloride with benzylbenzamide, is a yellow oil which boils at 180—200° under 20 mm. pressure; when heated under the ordinary pressure, it boils at 110°, being completely resolved thereby into benzonitrile and benzyl chloride, thus behaving in the manner characteristic of the iminochlorides, $CPhCl{\cdot}NR$, in which R is an aliphatic radicle.

2 : 3-*Diphenyl*-1-*benzylhydroxyamidine hydrochloride*,

$$C_7H_7{\cdot}N{:}CPh{\cdot}NPh{\cdot}OH,HCl,$$

obtained by mixing ethereal solutions of the foregoing iminochloride and of phenylhydroxylamine, crystallises from absolute alcohol containing hydrochloric acid in lustrous needles and melts at 195°; the *base* is an easily decomposable oil which, on boiling with water, gives the odour of nitrosobenzene and is therefore not identical with 1 : 2-phenyl-3-benzylhydroxyamidine.

1 : 2-*Diphenyl*-3-p-*tolylhydroxyamidine*, $NPh{:}CPh{\cdot}N(OH){\cdot}C_6H_4Me$, obtained from *p*-tolylhydroxylamine and benzanilideimide chloride, melts at about 175°, crystallises from ethyl acetate on adding light petroleum in bright yellow, felted needles, and gives a *hydrochloride* melting at 185°.

2 : 3-*Diphenyl*-1-p-*tolylhydroxyamidine*, $C_6H_4Me{\cdot}N{:}CPh{\cdot}NPh{\cdot}OH$, melts at 191°, forms darker yellow needles, and is less soluble than its isomeride, whilst its *hydrochloride* melts at 201—202°, producing a violet coloration.

Both 1 : 2-diphenyl-3-*p*-tolylhydroxyamidine and 2 : 3-diphenyl-1-*p*-tolylhydroxyamidine give the same 1 : 2-diphenyl-3-*p*-tolylamidine (m. p. 135—136°; hydrochloride, m. p. 243—244°; Marckwald gives 133° and 237°) on reduction with sulphur dioxide in absolute alcoholic solution. Measurements of the conductivities of the hydrochlorides of 1 : 2-diphenyl-3-*p*-tolylhydroxyamidine and of 1 : 2-diphenyl-3-*p*-tolylamidine indicate that salts of the former are much more hydrolysed than those of the latter base, and show the acidifying influence of the hydroxyl group. W. A. D.

Phenylazoethane. EUGEN BAMBERGER and WILHELM PEMSEL (*Ber.*, 1903, 36, 53—57).—Phenylazoethane, $NPh{:}NEt$, when mixed with amyl nitrite, is converted by hydrochloric acid into methylformazyl, $Ph{\cdot}N{:}N{\cdot}CMe{:}N{\cdot}NHPh$; apparently the acid brings about isomeric change into acetaldehydephenylhydrazone, and part of this becomes hydrolysed to phenylhydrazine and oxidised by the amyl nitrite to diazobenzene nitrate, which then condenses with the phenylhydrazone.

Diazobenzene hydroxide, in alkaline solution, converts phenylazoethane into phenylazoformazyl, NHPh·N:C(N:NPh)$_2$.

In presence of sodium ethoxide, phenylazoethane is converted by amyl nitrite into phenylazoacetaldoxime, NPh:N·CMe:N·OH; it is shown that sodium ethoxide brings about the isomeric change of phenylazoethane into acetaldehydephenylhydrazone, this is probably converted into the nitroso-derivative, NHPh·N:CMe·NO, and then by transformation into the *iso*nitroso-compound formulated above.

T. M. L.

Nitroso-, *iso*Nitroso-, and Nitro-derivatives of Aldehydehydrazones. EUGEN BAMBERGER and WILHELM PEMSEL. (*Ber.*, 1903, 36, 57—84).—In the absence of alkalis, aldehydrazones yield true nitroso-derivatives of the type R·C(NO):N·NHPh, which are converted by alkalis into the isomeric azo-oximes, R·C(:NOH)·N:NPh, are oxidised by nitrous acid to nitro-hydrazones, R·C(NO$_2$):N·NHPh, and readily lose NO, yielding products formed by the condensation of two radicles, –CR:N·NHPh.

Nitrosobenzylidenephenylhydrazine, NO·CPh:N·NHPh, could not be isolated; in the absence of alkalis, amyl nitrate converts the benzylidenephenylhydrazine into dibenzylidenediphenylhydrotetrazone,

$N_2Ph_2(N{:}CHPh)_2$,

and nitrobenzylidenephenylhydrazine, NO$_2$·CPh:N·NHPh. In presence of sodium ethoxide, the products are α-benzilosazone,

$C_2Ph_2({:}N{\cdot}NHPh)_2$,

and *benzeneazobenzaldoxime*, OH·N:CPh·N:NPh; the latter crystallises from benzene or light petroleum in minute, orange-yellow, felted needles with bronze-like lustre and from dilute alcohol in orange-red, silky needles, melts and intumesces at 134—135° (all melting points are corrected), and dissolves in alkali hydroxides; concentrated sodium hydroxide precipitates the sodium salt as a yellow, crystalline paste. The *benzoyl* derivative, OBz·N:CPh·N:NPh, crystallises from light petroleum in glistening, red, flat needles, and melts at 126—126·5°. In presence of pyridine, amyl nitrite again yields the oxime.

Benzeneazoanisaldoxime, OMe·C$_6$H$_4$·C(:NOH)·N:NPh, prepared from anisaldehydephenylhydrazone and amyl nitrite in presence of sodium ethoxide or pyridine, crystallises from benzene in minute, felted, silky, orange-yellow needles, melts and intumesces at 147°, and dissolves in alkali hydroxides; the *sodium* salt is precipitated in yellow, flocculent crystals by concentrated sodium hydroxide. The *benzoyl* derivative crystallises from light petroleum in transparent, orange-red tablets and melts at 129—129·5°. A by-product, insoluble in alkalis, was identified as dehydroanisylidenephenylhydrazine,

$OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NPh{\cdot}C({:}N{\cdot}NHPh){\cdot}C_6H_4{\cdot}OMe$,

a condensation product formed by loss of NO from two molecules of the initial nitrosohydrazone. *Nitrosoanisaldehydephenylhydrazone*,

$OMe{\cdot}C_6H_4{\cdot}C(NO){:}N{\cdot}NHPh$,

prepared from anisaldehydephenylhydrazone and amyl nitrite in the absence of alkalis, forms long, golden-yellow, felted, silky needles and decomposes at 69·5°; sodium ethoxide and pyridine convert it into the isomeric oxime, whilst nitrous fumes oxidise it to the nitro-compound

$OMe\cdot C_6H_4\cdot C(NO_2)\colon N\cdot NHPh$, which is rapidly decomposed by sodium methoxide into sodium nitrite and dianisyldiphenyltetrazoline,

$$OMe\cdot C_6H_4\cdot C{<}^{N\cdot NPh}_{NPh\cdot N}{>}C\cdot C_6H_4\cdot OMe.$$

Benzeneazo-m-*nitrobenzaldoxime*, $NO_2\cdot C_6H_4\cdot C(\colon NOH)\cdot N\colon NPh$, crystallises from alcohol or benzene in cream-coloured needles and decomposes at 183°. The *benzoyl* derivative crystallises from benzene in stout, glassy, ruby-red prisms, and from a mixture of benzene and light petroleum in rose-coloured, silky, felted needles, and decomposes at 153°. *Nitroso* m-*nitrobenzylidenephenylhydrazine*,

$$NO_2\cdot C_6H_4\cdot C(NO)\colon N\cdot NHPh,$$

is a yellow, crystalline powder, which decomposes and intumesces at 98·5°, and by sodium ethoxide or pyridine is converted into the isomeric oxime.

a-m-*Dinitrobenzylidenephenylhydrazine*, $NO_2\cdot C_6H_4\cdot C(NO_2)\colon N\cdot NHPh$, separates from alcohol in ruby-red, glistening needles with a pale green, metallic lustre, and from a mixture of benzene and alcohol in thin flakes, and decomposes with frothing at 140·5°.

Benzeneazo-p-*nitrobenzaldoxime*, $NO_2\cdot C_6H_4\cdot C(\colon NOH)\cdot N\colon NPh$, crystallises from benzene in minute, golden-yellow, glistening needles and intumesces and melts at 180·8°. *Nitroso*-p-*nitrobenzylidenephenylhydrazine*, $NO_2\cdot C_6H_4\cdot C(NO)\colon N\cdot NHPh$, decomposes with frothing at 79° and is converted by pyridine into the isomeric oxime.

a-p-*Dinitrobenzylidenephenylhydrazine*,

$$NO_2\cdot C_6H_4\cdot C(NO_2)\colon N\cdot NHPh,$$

crystallises from benzene in glistening, greenish-golden, or dark orange-red needles with a bronze-like lustre, and melts and intumesces at 156·5°.

a-*Nitroso*-o-*nitrobenzylidenephenylhydrazine*,

$$NO_2\cdot C_6H_4\cdot C(NO)\colon N\cdot NHPh,$$

intumesces and decomposes at 83·5—84° and is converted by pyridine into the isomeric *benzeneazo*-o-*nitrobenzaldoxime*,

$$NO_2\cdot C_6H_4\cdot C(\colon NOH)\cdot N\colon NPh,$$

which crystallises in clear, orange-yellow, silky, felted needles, and melts and intumesces at 153·5—154°. a-o-*Dinitrobenzylidenephenylhydrazine*, $NO_2\cdot C_6H_4\cdot C(NO_2)\colon N\cdot NHPh$, prepared only from *o* nitrophenylnitromethane and diazonium acetate, crystallises from alcohol in orange-yellow needles with a bronze-like lustre and melts at 146°.

T. M. L.

Acetaldehydephenylhydrazone. EUGEN BAMBERGER and WILHELM PEMSEL (*Ber.*, 1903, 36, 85—89).—The action of amyl nitrite on acetaldehydephenylhydrazone, either alone or in presence of pyridine or sodium ethoxide, yields phenylazoacetaldoxime,

$$CMe(\colon NOH)\cdot N\colon NPh,$$

and not the labile isomeric nitroso-derivative. Sodium diazoxide converts the hydrazone into methylformazyl, $NPh\colon N\cdot CMe\colon N\cdot NHPh$.

Acetaldehydephenylhydrazone can be prepared by adding ice-cold acetaldehyde to a solution of phenylhydrazine in ether cooled in a freezing mixture; the hydrazone which separates is quite white, and does not require distillation under reduced pressure. T. M. L.

Methyl Benzeneazobenzylidenenitronate. EUGEN BAMBERGER (*Ber.*, 1903, 36, 90—91).—When phenylnitroformaldehydehydrazone, $CPh \cdot C(NO_2) \vdots N \cdot NHPh$, is dissolved in ether and treated with diazomethane, *methyl benzeneazobenzylidenenitronate*,

$$OMe \cdot NO \vdots CPh \cdot N \vdots NPh,$$

is produced; it forms minute, orange-red needles, melts at 92°, and, when boiled with light petroleum or alcohol, is decomposed into benzeneazobenzaldoxime and formaldehyde. T. M. L.

Action of Amyl Nitrite on Phenylmetanitrobenzylidenehydrazine. EUGEN BAMBERGER and WILHELM PEMSEL (*Ber.*, 1903, 36, 92—101. Compare Minunni, Abstr., 1898, i, 190).—The following compounds were obtained by the action of amyl nitrite on phenyl-*m*-nitrobenzylidenehydrazine. (1) The *compound* $C_{26}H_{20}O_4N_6$ forms lemon-yellow, silky, felted needles and melts and intumesces at 166°. (2) The *compound* $C_{26}H_{20}O_4N_6$ crystallises from xylene in canary-yellow prisms and melts at 216—217°. (3) The *compound* $C_{26}H_{20}O_4N_6$ (?), which is also produced by prolonged boiling of (2) with benzene or acetic acid, crystallises from a mixture of chloroform and alcohol in flakes and melts at 212—213°. (4) The *compound* $C_{26}H_{20}O_4N_6$ crystallises from xylene in orange-yellow needles with $\frac{1}{2}C_8H_{10}$ and melts at 265°. (5) Phenyl-α-*m*-dinitrobenzylidenehydrazone,

$$NO_2 \cdot C_6H_4 \cdot C(NO_2) \vdots N \cdot NHPh.$$

(6) The *compound* $C_{20}H_{13}O_4N_5$, perhaps dinitrotriphenylosotriazole, $NPh<\begin{matrix} N \vdots C \cdot C_6H_4 \cdot NO_2 \\ | \\ N \vdots C \cdot C_6H_4 \cdot NO_2 \end{matrix}$, crystallises from chloroform in reddish-brown needles with bronze-like lustre and melts at 174—175°. The first four compounds are probably formed by the elimination of 2NO from 2 mols. of nitroso-*m*-nitrobenzylidenephenylhydrazine, and most of the six products were identified in the mixture obtained on decomposing the nitroso-compound with boiling ether. T. M. L.

Behaviour of Benzaldehydephenylhydrazone towards Nitrous Acid and Amyl Nitrite. EUGEN BAMBERGER and WILHELM PEMSEL (*Ber.*, 1903, 36, 347—358. Compare Bamberger and Grob, Abstr., 1901, i, 296, and 567).—*Nitrosobenzaldehyde*-p-*nitrophenylhydrazone*, $NO \cdot CPh \vdots N \cdot NH \cdot C_6H_4 \cdot NO_2$, prepared by the action of nitrous fumes on benzaldehydephenylhydrazone, or of nitrous acid or amyl nitrite on benzaldehyde-*p*-nitrophenylhydrazone, forms minute, golden-yellow, glistening needles and decomposes at about 94—95°. When boiled with alcohol, it loses nitric oxide yielding a *compound*, $NO_2 \cdot C_6H_4 \cdot N(N \vdots CHPh) \cdot CPh \vdots N \cdot NH \cdot C_6H_4 \cdot NO_2$, by condensation of 2 molecules; this separates from pyridine in golden-yellow crystals, melts at 238°, and is slightly soluble in the ordinary organic solvents. Amyl nitrite converts it into the nitrohydrazone (Bamberger and Grob, *loc. cit.*), but di-*p*-nitrotetraphenyltetrazoline,

$$NO_2 \cdot C_6H_4 \cdot N<\begin{matrix} CPh \vdots N \\ N \vdots CPh \end{matrix}>N \cdot C_6H_4 \cdot NO_2,$$

is also produced. Sodium ethoxide removes the nitroso-group and

converts it into benzaldehyde-*p*-nitrophenylhydrazone, whilst pyridine converts it into the isomeric p-*nitrobenzeneazobenzaldoxime*,

$$OH\cdot N:CPh\cdot N:N\cdot C_6H_4\cdot NO_2,$$

which crystallises from benzene with $\frac{1}{3}C_6H_6$ in red, silky, felted needles, and intumesces and melts at 142·5°. T. M. L.

Action of Amyl Nitrite on Anisaldehydephenylmethylhydrazone. Eugen Bamberger and Wilhelm Pemsel (*Ber.*, 1903, 36, 359—374).—*Anisaldehydephenylmethylhydrazone*,

$$OMe\cdot C_6H_4\cdot CH:N\cdot NMePh,$$

separates from alcohol in white needles and melts at 113·5—114°. A nitroso-derivative could not be prepared, but amyl nitrite gave a *nitroanisaldehydephenylmethylhydrazone*, $OMe\cdot C_6H_4\cdot C(NO_2):N\cdot NMePh$, which separates from ether or alcohol in thick, glistening, orange-yellow prisms, or in minute, lemon-yellow, felted needles, intumesces and melts at 104·7—105·2°, and has a normal molecular weight in a boiling solution of acetone. When boiled with alcohol, the NO_2 group is replaced by OH, and *β-anisoyl-α-phenyl-α-methylhydrazine*, $OMe\cdot C_6H_4\cdot CO\cdot NH\cdot NMePh$, is produced; this crystallises from acetic acid in minute, woolly, white needles, melts and decomposes at 165—166·5°, and has a normal molecular weight when dissolved in boiling acetone. Amyl nitrite eliminates the methyl group from this compound and gives *β-anisoyl-α-phenylnitrosohydrazine*, $OMe\cdot C_6H_4\cdot CO\cdot NH\cdot NPh\cdot NO$, which crystallises from a mixture of acetone and water in pale yellowish, almost colourless, silky needles, melts with liberation of gas at 123°, and rapidly decomposes when kept; the same substance is produced by the action of amyl nitrite on β-anisoylphenylhydrazine.

By reducing nitroanisaldehydephenylmethylhydrazone with zinc dust and acetic acid, anisonitrile, $OMe\cdot C_6H_4\cdot CN$, methylaniline, and *p*-methoxybenzylamine, $OMe\cdot C_6H_4\cdot CH_2\cdot NH_2$, are produced, together with a *polymeride* of *anisaldehydephenylmethylhydrazone*, which melts at 106·5—108·5°, cannot be obtained in a crystalline form, and dissolves neither in acids nor in alkalis. Sodium methoxide converts the nitrohydrazone, by elimination of the nitro-group, into *dianisyldiphenyltetrazoline*, $OMe\cdot C_6H_4\cdot C{<}{\substack{N\cdot NPh\\ NPh\cdot N}}{>}C\cdot C_6H_4\cdot OMe$, which crystallises from acetic acid in transparent, glistening, flat prisms having an orange-yellow to orange-red colour, and melts at 173·5—174·5°.

Anisaldehydenitrophenylmethylhydrazone,

$$OMe\cdot C_6H_4\cdot CH:N\cdot NMe\cdot C_6H_4\cdot NO_2,$$

a by-product of the action of amyl nitrite on anisaldehydephenylmethylhydrazone, crystallises from alcohol in minute, golden-yellow, silky needles and melts at 159—159·5°.

m-*Nitrobenzaldehydephenylmethylhydrazone*,

$$NO_2\cdot C_6H_4\cdot CH:N\cdot NMePh,$$

crystallises from alcohol in orange-red needles and melts at 112—113°. T. M. L.

2 : 5-Dimethylbenzyl-2 : 5-dimethylbenzylidenehydrazine. Everhart Percy Harding and Edgar W. Rice (*J. Amer. Chem. Soc.*, 1902, 24, 1066—1068).—2 : 5-*Dimethylbenzyl*-2 : 5-*dimethylbenzylidenehydrazine*, $C_6H_3Me_2\cdot CH_2\cdot NH\cdot N:CH\cdot C_6H_3Me_2$, prepared by the reduc-

tion of 2 : 5-dimethylbenzaldazine in alcoholic solution with 4 per cent. sodium amalgam, melts at 74—78° and is easily soluble in most organic solvents. Its *acetyl* derivative crystallises in long, white, satin-like needles melting at 137°, and the *benzoyl* derivative forms similar crystals melting at 134—134·5°. E. F. A.

2 : 4 : 6-Trimethylbenzaldazine. EVERHART PERCY HARDING (*J. Amer. Chem. Soc.*, 1902, **24**, 1068—1070).—2 : 4 : 6-*Trimethylbenzaldazine*, $N_2(:CH\cdot C_6H_2Me_3)_2$, prepared from 2 : 4 : 6-trimethylbenzaldehyde and hydrazine sulphate, crystallises from acetic acid in yellow prisms melting at 167°. On reduction with sodium amalgam, 2 : 4 : 6-*trimethylbenzyl*-2 : 4 : 6-*trimethylbenzylidenehydrazone*, melting at 88—89°, is formed. This yields an *acetyl* derivative melting at 155° and a *benzoyl* derivative melting at 142·5—143°, both crystallising in long, satin-like needles.

The nitroso-derivative, $C_6H_2Me_3\cdot CH_2\cdot N(NO)\cdot N:CH\cdot C_6H_2Me_3$, obtained from the hydrazone, forms long, yellow crystals melting at 117°. E. F. A.

Melting Points of *as*-Diphenylthiocarbamides. CARL KJELLIN (*Ber.*, 1903, **36**, 194—197).—When *as*-monohalogendiphenylthiocarbamides are treated in alcoholic solution with aniline in the cold, diphenylthiocarbamide and probably dihalogendiphenylthiocarbamides are formed. The asymmetrical thiocarbamides suffer a similar change when they are melted, or their alcoholic solutions boiled, diphenylthiocarbamide being always formed. *as*-Diphenylcarbamides decompose in the same manner. o-*Bromodiphenylthiocarbamide*, prepared from phenylthiocarbimide and *o*-bromoaniline, crystallises in silky needles melting at 161°, or, when heated slowly, at 144°; the crystals which separate from its solution in ethyl alcohol melt at 151° and contain diphenylthiocarbamide. The m-*bromo*-derivative, prepared in a similar manner, crystallises in needles melting indefinitely at 120°, and when crystallised from alcohol gives a product which melts at about 100°. The m-*chloro*-compound behaves similarly, crystallising in prisms or needles melting indefinitely at 120°. The *o*-chloro-compound forms prisms melting at 165°, but on heating or recrystallising the melting point falls to 145—150°; the diphenylthiocarbamide can be isolated in this case. p-*Chlorodiphenylthiocarbamide* crystallises in plates melting at 152°, and is far more stable. *m*-Nitrophenyldithiocarbamide melts at 155°, but soon changes into a mixture melting at 145°. *Di*-m-*bromodiphenylthiocarbamide* forms long needles melting at 135°, *di*-m-*chlorodiphenylthiocarbamide* prisms or needles, and *di*-o-*chlorodiphenylthiocarbamide* short prisms melting at 141°. These symmetrical compounds are quite stable and can be recrystallised. K. J. P. O.

Electrolytic Reduction of Acetylacetonedioxime. Dimethylpyrrazolidine. JULIUS TAFEL and EPHRAIM PFEFFERMANN (*Ber.*, 1903, **36**, 219—224. Compare Harries and Haga, Abstr., 1898, i, 293; 1899, i, 562).—Pure acetylacetonedioxime melts at 150°; when boiled

with water for some time, or when heated at 140°, it becomes transformed into dimethyl*iso*oxazole.

The dioxime was reduced in 30 per cent. sulphuric acid solution in the closed vessel previously described (Abstr., 1900, ii, 588). The conditions being concentration, 100 grams in 1 litre; current density, 120 amperes; cathode surface, 10 sq. dm. per litre; time, 2 hours, 40 minutes; temperature, −7° to 0°. The product obtained, *dimethylpyrrazolidine*, $CH_2<\begin{matrix}CHMe\cdot NH \\ CHMe\cdot NH\end{matrix}$, boils at 40—41° under 13·5 mm. pressure and at 141—143° under 746° mm., and solidifies at −7° to −6°. Its aqueous solution has strongly alkaline properties and reduces hot Fehling's solution. It is a diacidic base and its normal salts have a strongly alkaline reaction to litmus.

The *sulphate*, $C_5H_{14}N_2SO_4,2H_2O$, crystallises in colourless prisms, the *hydrochloride* is readily soluble in water, sparingly so in alcohol, the *picrate* melts and decomposes at 129—130°. The base forms an *additive* product with acetone, $C_8H_{18}ON_2$, melting at 68—69°, and volatile at the ordinary temperature. The *dibenzoyl* derivative crystallises in colourless prisms melting at 204·5° (uncorr.).

2 : 4-Diaminopentane is also formed in the electrolytic reduction of the dioxime. J. J. S.

5-Chloro-4-benzoyl-1-phenyl-3-methylpyrazole and a Bipyrazole. AUGUST MICHAELIS and FRITZ BENDER (*Ber.*, 1903, **36**, 523—530).—*5-Chloro-4-benzoyl-1-phenyl-3-methylpyrazole*, obtained when Nef's benzoylphenylmethylpyrazolone (Abstr., 1892, 146) is heated with phosphorus oxychloride for 5 hours at 125°, crystallises from alcohol in needles melting at 88° and distils at 245° under 15 mm. pressure. The same compound is obtained when 4 : 5-dibenzoyl-1-phenyl-3-methylpyrazolone is heated with phosphorus oxychloride. Phosphorus pentachloride transforms the benzoyl derivative into 4 : 5-dichloro-1-phenyl-3-methylpyrazole melting at 56° (Abstr., 1899, i, 942). Concentrated aqueous ammonia, at 150—160°, converts the chloropyrazole into *5-amino-4-benzoyl-1-phenyl-3-methylpyrazole*, which crystallises in colourless needles melting at 153°. The *hydrochloride*, $COPh\cdot C_3N_2MePh\cdot NH_2,HCl$, melts at 190°. The corresponding *anilino*-derivative, obtained by the action of aniline on the chloro-compound at 200°, melts at 171°, and is readily soluble in alcohol and ether, or concentrated hydrochloric acid. The *dipropylamino*-derivative,

$$COPh\cdot C_3N_2MePh\cdot NPr_2,$$

crystallises in colourless needles.

Alcoholic potash under pressure converts the chloro- compound into Nef's 4-benzoyl-1-phenyl-3-methyl-5-pyrazolone, which probably has the enolic structure.

The *phenylhydrazone* of chlorobenzoylphenylmethylpyrazole,

$$PhC(:N_2HPh)\cdot C_3N_2ClMePh,$$

crystallises in yellowish cubes, melts at 176°, and is only sparingly soluble in alcohol.

1 : 4-*Diphenyl-3-methyldipyrazole*, $N<\begin{matrix}NPh\cdot C-NH \\ CMe-C\cdot CPh\end{matrix}>N$, is obtained

when the chloropyrazole is heated with hydrazine hydrate (50 per cent.) for 12 hours at 180—200°; it crystallises from hot alcohol in felted needles melting at 232°, is sparingly soluble in water or glacial acetic acid, and has feebly acidic properties. The *silver* derivative forms a flocculent precipitate, the *acetyl* derivative melts at 174°, the *benzoyl* derivative at 166°, and the *methiodide* at 221°. When the dipyrazole is dissolved in fuming nitric acid and the solution poured into water, 1-*phenyl*-4-*nitrophenyl*-3-*methyldipyrazole* is formed; it has a yellow colour and melts above 300°. The corresponding *bromo*-derivative has also been obtained.

1 : 4-*Diphenyl*-3 : 6-*dimethyldipyrazole*, $N{<}{\begin{smallmatrix}NPh\cdot C\cdot NMe\\ \| \\ CMe-C-CPh\end{smallmatrix}}{>}N$, obtained by the action of sodium ethoxide and methyl iodide on the monomethyl compound, crystallises from alcohol in needles, melts at 163°, does not dissolve in alkalis, but is soluble in dilute hydrochloric acid; its *methiodide* melts at 205°.

A *compound*, $C_{34}H_{28}O_2N_6$, is obtained when benzoylphenylmethylpyrazolone is heated with hydrazine hydrate in sealed tubes. It crystallises in needles, melts above 300°, and is probably an azoimide.

Himmelbauer's acetylphenylmethylpyrazolone (Abstr., 1897, i, 114) behaves as a 5-acetoxypyrazole, as on treatment with phosphorus oxychloride it yields chlorophenylmethylpyrazole and acetyl chloride. The butyryl derivative behaves in a precisely similar manner.

J. J. S.

Action of *iso*Valeraldehyde on Antipyrine. David C. Eccles (*J. Amer. Chem. Soc.*, 1902, **24**, 1050—1052).—iso*Valeryldiantipyrine*, $C_4H_9\cdot CH(C_3N_2OMe_2Ph)_2$, obtained by heating *iso*valeraldehyde (1 mol.) and antipyrine (2 mols.) in presence of a small quantity of hydrochloric acid in a reflux apparatus for 6 hours at 100°, separates from light petroleum in white crystals melting at 160—161°.

E. F. A.

Synthesis of Pyridazine Derivatives. I. Carl Paal and Emil Dencks (*Ber.*, 1903, **36**, 491—497. Compare Abstr., 1901, i, 148, 154).—6-Phenyl-3-methylpyridazine may be obtained by the action of hydrazine hydrate on phenacylacetone. The original product is a thick, red-coloured oil, which, when kept or when distilled under reduced pressure, yields crystals of the phenylmethylpyridazine, probably by the elimination of 2 atoms of hydrogen. This crystallises in colourless needles, melts at 104—105°, and is readily soluble in most organic solvents, also in dilute mineral acids. The *hydrochloride*, *platinichloride* melting at 195—197°, *chromate*, $C_{11}H_{10}N_2,H_2CrO_4$, melting at 118—120°, and *mercurichloride* melting at 184—185° have been prepared.

On oxidation with dilute nitric acid at 150—160°, it yields 3-*phenylpyridazine*-6-*carboxylic acid*, $C_4N_2H_2Ph\cdot CO_2H$, which crystallises in colourless needles melting at 130—131°.

3 : 6-Diphenyldihydropyridazine cannot be obtained pure by the action of hydrazine hydrate on *s*-dibenzoylethane, as it is readily oxidised by the atmospheric oxygen to diphenylpyridazine. When diphenylpyridazine is reduced with alcohol and sodium, it yields a

dihydro-derivative melting at 202°; as this is apparently somewhat more stable than the dihydro-compound obtained synthetically, it is probably an isomeride. It is rapidly oxidised in solution, but only slowly in the solid state, and does not yield an acetyl derivative.

J. J. S.

Pyridazine Derivatives. II. CARL PAAL and JEAN UBBER (*Ber.*, 1903, 36, 497—512. Compare preceding abstract, also T. Gray, Trans., 1901, 79, 682; Smith and McCoy, Abstr., 1902, 645).—Ethyl 3 : 6-dimethyl-4 : 5-dihydropyridazine-4 : 5-dicarboxylate (compare Curtius, Abstr., 1895, i, 246; and Bülow, this vol., i, 196) cannot be hydrolysed to the corresponding acid. When left in contact with alcoholic potash (2 mols.) at the winter temperature, it yields the *potassium* salt of the acid ester together with Bülow's ethyl dimethyldihydropyridazinecarboxylate.

The *acid ester*, $CO_2H\cdot C_4N_2H_2Me_2\cdot CO_2Et$, crystallises in glistening, white plates, melts at 108—110°, and in small quantities may be distilled without undergoing decomposition. When kept in stoppered vessels, it slowly decomposes.

When the normal ester is hydrolysed with baryta water and the product oxidised with hydrogen peroxide, 3 : 6-*dimethylpyridazine*, $CMe{<}{N\!-\!\!-\!\!N \atop CH:CH}{>}CMe$, is obtained in the form of a solid melting at 24—33° and distilling at 210—216°; it is extremely hygroscopic and yields a hygroscopic *hydrochloride*. It forms two *aurichlorides*, the one, $(C_6H_8N_2,HCl)_2AuCl_3$, obtained in alcoholic solution crystallises in golden-yellow plates melting at 110—112°, and in contact with water is transformed into the salt, $C_6H_8N_2,HAuCl_4$; this is first deposited as an oil, but slowly solidifies and then melts at 175°.

Curtius's ester, when hydrolysed with 5 per cent. hydrochloric acid, yields small amounts of hydrazine and dimethylpyridazine, and when oxidised in acetone solution with permanganate yields *ethyl* 3 : 6-*dimethylpyridazine*-4 : 5-*dicarboxylate*, $C_4N_2Me_2(CO_2Et)_2$. This crystallises from dilute alcohol in flat needles, is readily soluble in most organic solvents and in mineral acids, and yields a crystalline compound with mercurichloride, $C_{12}H_{16}O_4N_2,HgCl_2$.

The *acid ester*, $CO_2H\cdot C_4N_2Me_2\cdot CO_2Et$, is produced in small quantities during the oxidation; it crystallises in colourless needles melting and decomposing at 155—156°. The free *acid*, $C_4N_2Me_2(CO_2H)_2$, obtained by the hydrolysis of the ester with alcoholic potash, or, still better, by the oxidation of the dihydro-ester with nitric acid and subsequent hydrolysis with baryta water, crystallises in colourless needles containing H_2O, melts and decomposes at 225—226°, is sparingly soluble in ether, chloroform, or benzene, and possesses only feebly basic properties; for example, it dissolves in concentrated hydrochloric acid, but is precipitated on dilution. The *potassium* salt,

$$C_8H_6O_4N_2K_2,3H_2O,$$

barium salt, with $3H_2O$, *silver* salt, $C_8H_6O_4N_2Ag_2$, *lead* salt, with $3H_2O$, *basic lead* salt, *copper* and *mercuric* salts have been prepared.

Ethyl 3 : 6-*dimethylpyridazinecarboxylate*, $C_4N_2HMe_2\cdot CO_2H$, crystallises in compact prisms melting at 55—57°.

J. J. S.

Some Anhydro-bases from Diamines of the Fatty Series. Tamemasa Haga and R. Majima (*Ber.*, 1903, 36, 333—339).—The products of the distillation of the hydrochlorides of tri- and tetramethylenediamines with anhydrous sodium acetate, the method devised by Ladenburg (Abstr., 1895, i, 73) for the preparation of the anhydrobase, ethenyldiamine, have been investigated. *Ethenyltrimethylenediamine* (*2-methyltetrahydropyrimidine*), $CH_2<\begin{matrix}CH_2\cdot CH_2\\NH\cdot CMe\end{matrix}\geqslant N$, is prepared by distilling a mixture of trimethylenediamine hydrochloride and sodium acetate at first under the ordinary, finally under reduced pressure; the oil thus obtained was fractionated under 20 mm. pressure, when the base distils at 170—200° (temperature of bath), and diacetyltrimethylenediamine above 270°; the base is purified by conversion into the *nitrate*, which melts at 109—110°; it forms crystals melting at 72—74° and boiling at 120—126° under 12 mm. pressure; the *oxalate* crystallises in hygroscopic, silky needles melting at 119°, the *picrate* in flattened prisms melting at 152°, the *platinichloride* in soluble, short, orange prisms melting and decomposing at 206—207°, and the *urate* in small, soluble octahedra. Diacetyltrimethylenediamine, $CH_2(CH_2\cdot NHAc)_2$, which crystallises in prisms melting at 101°, has been previously described by Strache (Abstr., 1888, 1172), who found the melting point 79°; it forms an *oxalate* crystallising in needles melting at 126°.

Diacetyltetramethylenediamine, $NHAc\cdot[CH_2]_4\cdot NHAc$, is obtained as the final fraction when tetramethylenediamine hydrochloride is distilled with anhydrous sodium acetate under 12 mm. pressure; it crystallises in small prisms melting at 137°. *Ethenyltetramethylenediamine*, $\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\|\\CH_2\cdot NH\cdot CMe\end{matrix}\geqslant N$, is contained in the first fraction in the distillation just mentioned, and was isolated as the *aurichloride*, which crystallises in small prisms melting at 157°; the *platinichloride* is readily soluble; the *picrate* forms short prisms melting at 138°.

K. J. P. O.

Tetra-alkylpiperazonium Compounds. D. Strömholm (*Ber.*, 1903, 36, 143—145).—According to Van Rijn (*Ned. Tidschr. Pharm.*, 1898, 10, 5), piperazine can only combine with three alkyl groups; in reality, tetra-alkyl derivatives can readily be prepared. *Tetramethylpiperazonium iodide*, $C_4H_8N_2Me_4I_2$, is prepared by the action of methyl iodide and aqueous sodium hydroxide on piperazine, and is also formed when the dimethyl derivative is heated with methyl iodide; it decomposes at about 300°. The *platinichloride*, $C_4H_8Me_4PtCl_6$, is a sparingly soluble precipitate. When the iodide is heated with silver oxide and water, decomposition occurs, and a base with reducing properties is formed. With methyl iodide in ethereal solution, diethylpiperazine yields a mixture of mono- and di-methyldiethylpiperazonium derivatives. *Dimethyldiethylpiperazonium iodide* is formed when diethylpiperazine is heated in aqueous solution with methyl iodide; it is more soluble in water than the tetramethyl compound, and yields a *platinichloride*, $C_4H_8N_2Me_2Et_2PtCl_6$, and *aurichloride* which are sparingly soluble in hot water; the picrate is insoluble in alcohol.

A. H.

Synthesis of Alkylketodihydroquinazolines. MARSTON TAYLOR BOGERT and WILLIAM FLOWERS HAND (*J. Amer. Chem. Soc.*, 1902, **24**, 1031—1050).—Bogert and Gotthelf have shown in previous papers (compare Abstr., 1900, i, 412, 608; and Gotthelf, Abstr., 1901, i, 764) that ketodihydroquinazolines may be prepared by heating together in sealed tubes anthranilic acid or its acyl derivatives with a nitrile. It is now shown that the same compounds are obtained by heating *a*-aminobenzonitrile in sealed tubes with the aliphatic anhydrides.

Even better yields and purer compounds are obtained by warming acyl-*o*-aminobenzonitriles with an alkaline solution of hydrogen peroxide.

Improved methods for the preparation of *o*-nitrobenzonitrile and *o*-aminobenzonitrile are described, as also the following new acyl derivatives of the latter.

Propionyl-o-aminobenzonitrile forms colourless, glassy prisms melting at 119°; the *butyl* derivative crystallises in glassy needles melting at 89—89·5°, the iso*butyl* derivative forms long, white, silky needles melting at 111—111·5°, and the iso*valeryl* derivative crystallises in needles and melts at 105·5—106·5°.

The series of 2-alkyl-4-ketoquinazolines, $C_6H_4<\begin{matrix}N{=}CR\\ CO{\cdot}NH\end{matrix}$, and their picrates are also fully described (compare Gotthelf, *loc. cit.*).

E. F. A.

Hydrazinodimethylnicotinic Acids and Indazole Derivatives from Lutidine. AUGUST MICHAELIS and K. VON AREND (*Ber.*, 1903, **36**, 515—522).—Ethyl chlorodimethylnicotinate (Abstr., 1902, 823) readily condenses with phenylhydrazine yielding 4-*phenylhydrazine-2:6-dimethylnicotinic acid*, $N<\begin{matrix}CMe\cdot C(CO_2H)\\ CMe{=\!=\!=}CH\end{matrix}>C\cdot NH\cdot NHPh$. It crystallises in small, yellow needles melting and decomposing at 176—177°, and is sparingly soluble in most solvents with the exception of aqueous alkalis. The *hydrochloride* is sparingly soluble in water and does not melt below 360°. When the acid is heated for some time at 130—140°, it yields an *anhydride*,

$$\begin{matrix}CMe{:}CH\cdot C\cdot NH\\ | \qquad\quad \| \\ N{:}CMe{-}C\cdot CO\end{matrix}>NPh,$$

in the form of a dark yellow powder melting at 233—234°. When this is crystallised from alcohol or chloroform it is partially transformed into the acid. When heated with methyl iodide for 12 hours at 150°, it yields the hydriodide of a *methyl* derivative,

$$\begin{matrix}CMe{:}CH\cdot C{=}N\\ | \qquad\quad | \\ NMe\cdot CMe{:}C\cdot CO\end{matrix}>NPh,$$

which is sparingly soluble in alcohol and melts at 261°. The *free* base, $C_{15}H_{15}ON_3$, crystallises in flat, pale yellow needles containing $3H_2O$; it begins to sinter at 68°, but in the anhydrous form melts sharply at 144°.

Hydrazinodimethylnicotinic anhydride, $\begin{matrix}CMe{:}CH\cdot C\cdot NH\\ | \qquad\quad \| \\ N{=}CMe\cdot C\cdot CO\end{matrix}>NH$, obtained by the action of hydrazine hydrate on ethyl chloromethylnicotinate at 150°, crystallises from water in plates containing H_2O.

It is sparingly soluble in cold water and in organic solvents, but dissolves in aqueous alkalis. The *platinichloride*,

$$(C_8H_9ON_3)_2,H_2PtCl_6,2H_2O,$$

forms red crystals and does not melt. When the anhydride is heated with methyl iodide at 150°, it yields *hydrazinomethyllutidonecarboxylic anhydride*, $\begin{matrix}\mathrm{CMe{:}CH\cdot C{=}N}\\ \mathrm{NMe\cdot CMe{:}C\cdot CO}\end{matrix}\!\!>\!\mathrm{NH,3H_2O}$, in the form of its *hydriodide*. The hydrated base melts at 92° and becomes anhydrous at 167°. The hydriodide melts at 255—256° and the *platinichloride* at 242°.

3-*Chloro-2-phenylindazole* from lutidine, $\begin{matrix}\mathrm{CMe{:}CH\cdot C\cdot N}\\ \mathrm{N{:}CMe{-}C\cdot CCl}\end{matrix}\!\!>\!\mathrm{NPh}$, obtained by the action of phosphorus oxychloride on phenylhydrazinodimethylnicotinic acid, forms colourless crystals, melts at 179—180°, and is insoluble in water. On reduction, it yields the phenylindazole of lutidine, which forms monohydrated, colourless needles melting at 150°; when anhydrous, it melts at 154°.

The *chloroindazole* of lutidine melts at 265—266° and is readily soluble in alcohol, benzene, or dilute acids (compare E. Fischer and Seuffert, Abstr., 1901, i, 411). J. J. S.

Phenyldiethyltriazine. CARL D. HARRIES (*Ber.*, 1903, **36**, 202—204).—The compound described by Bamberger and Tichvinsky as phenyldiethyltriazine (this vol., i, 131) is in reality ethylaniline, the oxalate of which melts at 113·5—114·5°. It has already been shown (Abstr., 1894, i, 284) that the products of reduction of the nitrosoamine of phenyldimethylhydrazine are methylhydrazine and methylaniline. J. J. S.

Action of Phenylhydrazine on Benzoyl-ψ-thiocarbamides. 3-Amino-1:5-diphenylpyrro-αβ′-diazole [3-Amino-1:5-diphenyl-1:2:4-triazole] Derivatives. HENRY L. WHEELER and ALLING P. BEARDSLEY (*Amer. Chem. J.*, 1903, **29**, 73—82).—It has been shown by Wheeler and Johnson (Abstr., 1902, i, 26) that the acyl-ψ-thiocarbamides readily react with phenylhydrazine to form aminotriazoles. By further experiments, it has been found that the triazoles formed from the benzoyl-ψ-thiocarbamides are 3-amino-1:5-diphenyl-1:2:4-triazoles.

Benzoylbenzyl-ψ-thiocarbamide, $\mathrm{NBz{:}C(S\cdot CH_2Ph)\cdot NH_2}$, obtained by the action of benzyl chloride on a solution of benzoylthiocarbamide in dilute potassium hydroxide, crystallises in white, glistening plates and melts at 161°. 3-*Amino*-1:5-*diphenyltriazole*, $\mathrm{NPh}\!<\!\begin{matrix}\mathrm{N{=}C\cdot NH_2}\\ \mathrm{CPh{:}N}\end{matrix}$, prepared by the action of phenylhydrazine on benzoylmethyl-ψ-thiocarbamide or on the benzyl compound just described, forms colourless prisms, melts at 154·5°, and is readily soluble in alcohol or hot benzene; its *picrate* melts at 183° and its *hydrochloride* at 205°. When treated with nitrous acid in presence of hydrochloric acid, it is converted into 3-chloro-1:5-diphenyltriazole identical with that obtained by Cleve (Abstr., 1897, i, 173) from hydroxy-1:5-diphenyltriazole. 3-*Benzoylamino*-1:5-*diphenyltriazole* crystallises from dilute alcohol or

benzene and melts at 159—160°; its *sulphate* melts at 195°. It is converted by hydrochloric acid into a *hydrochloride* which melts and effervesces at 205°; this salt is also formed when aminodiphenyltriazole is warmed with excess of benzoyl chloride without a solvent. 3-*Acetylamino*-1 : 5-*diphenyltriazole hydrochloride*, obtained by the action of acetyl chloride on the aminotriazole, forms a white powder and melts at 156—157°.

The constitution of these triazoles was established by the two following syntheses. *Dibenzoylphenylaminoguanidine*,

NPhBz·NH·C(NH)·NHBz,

melts and effervesces at 156°, and when boiled for 6 hours with absolute alcohol is converted into 3-benzoylamino-1 : 5-diphenyltriazole. When *as*-benzoylphenylhydrazine is warmed with ethyl benzoyliminodithiocarbonate, mercaptan is evolved and *phenyldibenzoylethyl-ψ-thiosemicarbazide*, NPhBz·NH·C(SEt):NBz, is produced, which crystallises from benzene in square plates and melts at 170—171°; if this substance is boiled with alcoholic ammonia, mercaptan is produced together with dibenzoylphenylaminoguanidine, which, under the conditions of the experiment, is converted into 3-benzoylamino-1 : 5-diphenyltriazole.

3-*Phenylamino*-1 : 5-*diphenyltriazole*, obtained by the action of phenylhydrazine on benzoylphenylethyl-ψ-thiocarbamide, crystallises from alcohol in white needles and melts at 202°. 3-*Benzoylphenylamino*-1 : 5-*diphenyltriazole* melts at 148—149°.

By the action of heat on a mixture of *as*-benzoylphenylhydrazine and benzoyl-*p*-tolylethyl-ψ-thiocarbamide, *dibenzoyl-p-tolylphenylaminoguanidine*, NPhBz·NH·C(NH·C_6H_4Me):NBz, is produced, which forms colourless needles and melts and decomposes at 279°; if this compound is boiled with dilute alcoholic potassium hydroxide, it is converted into 3-*p*-tolylamino-1 : 5-diphenyltriazole (Wheeler and Johnson, Abstr., 1902, i, 27) melting at 227—228°.

Benzoylphenyldimethyl-ψ-thiocarbamide, NBz:C(SMe)·NPhMe, obtained by the action of methylaniline on methyl benzoyliminodithiocarbonate, crystallises from alcohol in colourless prisms and melts at 113°. When treated with phenylhydrazine, it is converted into 3-*phenylmethylamino*-1 : 5-*diphenyltriazole*, which crystallises in lozenge-shaped plates and melts and effervesces at 202—203°. E. G.

Azoxybenzene. ARTHUR LACHMANN (*J. Amer. Chem. Soc.*, 1902, **24**, 1178—1200).—Azoxybenzene is best obtained by reducing nitrobenzene with a methyl-alcoholic solution of sodium hydroxide. The quantity of water present has no effect on the yield, but the presence of acetone is extremely detrimental. One hundred grams of light petroleum (b. p. 70—80°) dissolve 10·7 grams of azoxybenzene at 0° and 43·5 grams at 15°; 100 grams of 94 per cent. alcohol dissolve 5 grams at 0° and 11·4 grams at 15°. Azoxybenzene is very soluble in hot light petroleum.

By the action of sulphuric acid on azoxybenzene, *p*-hydroxyazobenzene and azobenzene are produced along with a black, amorphous powder, *p*-hydroxyazobenzene-*p*-sulphonic acid, and amylamine. The quantities of these products depend on various factors, amongst which

are mentioned the initial temperature of the mixture, the maximum temperature reached, the concentration of the acid, the ratio of acid to azoxybenzene, and the duration of the experiment. Since the reaction is exothermic, it should be carried out in a large vessel so as to permit of as much radiation as possible, otherwise it proceeds too violently. The method used to separate the products is described. By using a somewhat diluted acid (85 per cent.), keeping the temperature low, and taking 5 to 20 times as much sulphuric acid as azoxybenzene, 60 to 75 per cent. of the azoxybenzene is converted into *p*-hydroxyazobenzene. The proportion of *o*-hydroxyazobenzene formed is small; this is a red substance which is volatile in steam and melts at 81°. The amorphous, black powder does not seem to have a uniform composition; it contains nitrogen and appears to be a polymerisation product of high molecular weight; it is insoluble in all the common solvents and is infusible. Amylamine (probably normal) is only formed in small quantity; its production seems to be associated with that of the black powder and with the high temperature. Amylamine hydrochloride forms white needles which are soluble in water and alcohol, and gives a yellow, insoluble platinichloride. The *p*-hydroxyazobenzene-*p*-sulphonic acid is produced by simple sulphonation. The quantity of azobenzene produced varies from 30 to 60 per cent. of the azoxybenzene employed. Experiments indicate that the hydroxyazobenzene and the azobenzene are not formed simultaneously, but that the azobenzene is produced by auto-reduction of the hydroxyazobenzene. The main action of sulphuric acid on azoxybenzene is to transform it into hydroxyazobenzene, and the author is of the opinion that this is the result of a direct intramolecular rearrangement without the production of any intermediate compound.

p-Hydroxyazobenzene-*p*-sulphonic acid is not identical with the substance described by Wilsing (*Annalen*, 1882, **215**, 228). Its salts are extremely hygroscopic; the sodium salt crystallises with $2H_2O$ in yellow plates and requires for its dissolution 140 parts of water at 15°. When the acid or its salts are treated with bromine water, six atoms of bromine are taken up, tribromophenol is precipitated, and the solution contains phenolsulphonic acid. During this reaction, a diazonium salt is formed ($SO_3H \cdot C_6H_4 \cdot N \colon N \cdot C_6H_4 \cdot OH + 3Br_2 = C_6H_2Br_3 \cdot OH + SO_3H \cdot C_6H_4 \cdot N_2Br + 2HBr$), which is then hydrolysed ($SO_3H \cdot C_6H_4 \cdot N_2Br + H_2O = SO_3H \cdot C_6H_4 \cdot OH + N_2 + HBr$).

Azoxybenzene is not affected by heating in a current of hydrogen chloride, but when heated in a sealed tube with concentrated hydrochloric acid at 225° for 8 hours, it is completely changed, and the product contains phenol, aminophenol, and chloroaniline.

The action of hydroxylamine on azoxybenzene consists simply of reduction and is extremely slow. When heated with zinc ethyl, a gas is evolved containing ethylene and ethane, and the residue contains aniline and ethylaniline.

Hydrochloric acid acts readily on diphenylnitrosoamine, nitrosyl chloride being formed ($Ph_2N \cdot NO + HCl = Ph_2NH + NOCl$). With hydroxylamine, diphenylnitrosoamine gives diphenylamine and nitrous oxide, and with phenylhydrazine it enters into violent reaction,

nitrogen being liberated and a residue containing diphenylamine being obtained.

Azoxybenzene and diphenylnitrosoamine are isomerides, but as they behave so differently towards reagents it is concluded that there is no justification for attributing to azoxybenzene the constitution NPh:NPh:O, which has been suggested. The author believes that the properties of azoxybenzene are best indicated by the formula $O<\begin{matrix}NPh\\|\\NPh\end{matrix}$. J. McC.

New Decompositions of the Diazo-compounds. JOACHIM BIEHRINGER and ALBERT BUSCH (*Ber.*, 1903, 36, 135—137. Compare Abstr., 1902, i, 575).—The substances described as dibenzoyl derivatives of hydrazobenzene and the hydrazotoluenes are, in reality, benzaniline and the benzotoluidines formed by the action of the benzoyl chloride on portions of the free bases which had escaped diazotisation owing to the insolubility of their hydrochlorides under the conditions of the experiment (compare also Freundler, 1902, i, 697). A. H.

Benzoylation of the Hydrazo-compounds. JOACHIM BIEHRINGER and ALBERT BUSCH (*Ber.*, 1903, 36, 137—141).—When hydrazobenzene is treated with benzoyl chloride in presence of aqueous potash, the products consist of benzaniline, benzoylbenzidine, and *dibenzoylbenzidine*, which can be crystallised from nitrobenzene or phenol and melts at 347—350°. When the benzoylation is carried out in alcoholic solution and in presence of slaked lime, on the other hand, *benzoylhydrazobenzene* is formed, which crystallises in colourless plates melting at 138—139°. The dibenzoyl compound described by Freundler (Abstr., 1902, i, 697) could not be obtained. *Benzoyl*-p-*hydrazotoluene* crystallises in colourless, prismatic needles, and melts at 189°. The corresponding derivative of *o*-toluene could not be prepared.
A. H.

Simultaneous Oxidation and Reduction of Hydrazo-compounds. JOACHIM BIEHRINGER and ALBERT BUSCH (*Ber.*, 1903, 36, 339—341).—Hofmann showed that hydrazobenzene is changed into a mixture of azobenzene and aniline when heated above its melting point; similarly, acetylhydrazobenzene was found by Stern (Abstr., 1884, 1015) to be transformed by heat into acetanilide and azobenzene. It is now found that the same change is effected, but only to a small extent, by heating hydrazobenzene with alcohol under pressure at 120—130° for 6—8 hours. Hydrazobenzene and benzoic anhydride give benzanilide and azobenzene when heated together at 120° in alcoholic solution. *o*-Hydrazotoluene under the same conditions gives *o*-azotoluene and *o*-toluidine. *p*-Hydrazotoluene also yields *p*-azotoluene and *p*-toluidine, but *o*-aminoditolylamine (m. p. 107°) is obtained at the same time (compare Melms, *Ber.*, 1870, 3, 554; and Täuber, Abstr., 1892, i, 853).
K. J. P. O.

Isomeric Change in Benzene Derivatives. The Interchange of Halogen and Hydroxyl in Benzenediazonium Hydroxides. Kennedy J. P. Orton (*Proc. Roy. Soc.*, 1903, 71, 153—161).—The intramolecular change of *s*-trichloro- and *s*-tribromo-benzenediazonium hydroxides, $C_6H_2X_3 \cdot N(OH){:}N$, into hydroxybenzene derivatives by the interchange of the hydroxyl for one of the halogen atoms in the ortho-position has been studied. This takes place under all conditions under which the hydroxide can be present. The diazonium acetate undergoes change more readily than the nitrate or sulphate, because it is hydrolysed to a much greater extent; the transformation with the diazonium hydrogen carbonate is almost instantaneous. The author believes that the change consists in the transference of the atom attached to the nitrogen to the ortho-carbon atom of the nucleus, an ortho-quinone being formed.

s-*Trichlorobenzenediazonium hydrogen sulphate*, $C_6H_2Cl_3 \cdot N(SO_4H){:}N$, is obtained by diazotising *s*-trichloroaniline in glacial acetic acid and sulphuric acid with amyl nitrite; it is obtained in colourless, lustrous prisms which are readily soluble in water but insoluble in ether. The corresponding *nitrate*, $C_6H_2Cl_3 \cdot N(NO_3){:}N$, forms colourless needles. Both salts undergo a change when kept for two or three days, and then dissolve in water to a yellow solution from which silver chloride can be precipitated; after standing for 16 days, a solution of 0·5 gram of the hydrogen sulphate in 100 c.c. of water had decomposed to the extent of about 2 per cent. into the diazophenol. A solution of 1·75 grams of the diazonium nitrate in 150 c.c. of water with the molecular quantity of sodium acetate, when kept at 10—15° in the dark for 40 hours, changed to the extent of 54·5 per cent. into the diazophenol, and the change takes place even more quickly when sodium hydrogen carbonate is added to a solution of the diazonium nitrate. 3 : 5-*Dichloro*-o-*diazophenol* (3 : 5-*dichloro*-o-*diazoquinone*), $N_2{:}C_6H_2Cl_2{:}O$, obtained in this way, is purified by means of the *hydrochloride*, $O{:}C_6H_2Cl_2{:}N_2,HCl$, which decomposes with water. The diazophenol forms orange prisms which melt at 83—84°; it is easily soluble in the ordinary solvents and is decomposed by hot water. In concentrated acids, it gives a colourless solution which becomes yellow on dilution, and under these conditions couples with β-naphthol. During the decomposition of the diazonium salts, a yellow, amorphous substance is produced; this may be a hydroxyazo-compound, but its composition has not been settled.

s-*Tribromobenzenediazonium nitrate*, $C_6H_2Br_3 \cdot N(NO_3){:}N$, when first prepared, is white, but on keeping it acquires a yellow colour. It undergoes a change quite similar to that suffered by the corresponding chloro-compound. When sodium acetate is added to a solution of the salt, a yellow deposit is obtained, consisting of yellow crystals mixed with a yellow, amorphous powder, which may be removed by shaking with water and decanting before the light powder has time to settle. These crystals are 3 : 5-*dibromo*-o-*diazophenol* (or -*diazoquinone*), $O{:}C_6H_2Br_2{:}N_2$, which explodes when heated at 140°, is very soluble in chloroform, benzene, ether, acetic acid, or hot alcohol, but only sparingly so in cold water. Concentrated acids dissolve it to a colourless solution, and in such solution it couples with β-naphthol. The

hydrochloride is obtained by passing hydrogen chloride into an ethereal solution. The amorphous, yellow powder obtained at the same time as the diazophenol appears to be similar to that produced from *s*-trichlorobenzenediazonium salts.

It has further been found that a similar interchange of halogen for hydroxyl takes place readily in solutions of chloro- and bromo-naphthalenediazonium salts. J. McC.

Reaction between Amines and Nitrous Acid. Hans Euler (*Annalen*, 1902, 325, 292—304).—Measurements of the rate of decomposition of diazonium salts into phenols and nitrogen have been made either by measuring the nitrogen evolved or by titrating the acid formed during the change. Very concordant values for the velocity-coefficient were thus obtained; for benzenediazonium chloride at 25°, K is about 0·00122. The velocity of the reaction is not affected by allowing the nitrogen to be given off under considerable pressure, or by the presence of excess of acid, at least in dilute aqueous solution, or by the presence of neutral salts. In aqueous solution, the rate of decomposition is independent of the anion.

When dissolved in aqueous or pure alcohol, the rate of decomposition of the diazonium salts into benzene derivatives and nitrogen is, on the other hand, greatly affected by the presence of acids; thus, the addition of hydrobromic acid to an aqueous (75 per cent.) alcoholic solution of *p*-bromobenzenediazonium bromide, or of hydrochloric acid to the corresponding chloride, greatly diminishes the rate of decomposition. The product of decomposition, both in the presence and in the absence of excess of acid, is mainly bromobenzene. Hantzsch (Abstr., 1902, i, 329) found, however, that the rate of decomposition of *s*-tribromobenzenediazonium sulphate into *s*-tribromobenzene in dilute (5 per cent.) alcoholic solution was not affected by the presence of excess of sulphuric acid. In aqueous alcoholic solution, therefore, the rate of decomposition of diazonium salts is dependent on the nature of the anion.

Hantzsch (Abstr., 1900, i, 703) has come to the conclusion that the typical diazo-decompositions are not a cleavage of the diazonium, Ar·N(A)⋮N, but of the diazo-, Ar·N:N(A), compounds; if this be the case, then the rate of formation of a phenol, which arises, according to Hantsch, by a decomposition of the "*syn*"-diazobenzene hydroxide, should be largely decreased by excess of acid; but the rate of decomposition is independent of the amount of acid present. Further, as the diazo-haloids, and more especially the diazo-cyanides (Hantzsch, *loc. cit.*), have a great tendency to pass into the "*syn*"-diazo-form, the rate of decomposition of these compounds should show a progressive increase from chlorides to cyanides; such, however, is not the case; the rate of decomposition is independent of the anion.

The temperature-coefficient of the phenol-cleavage seems to vary little in the various diazonium salts.

Substituent groups in the benzene nucleus, such as the methoxy- or carboxy-groups and the halogens, chlorine, and bromine, all decrease the rate of the phenol cleavage; a methyl group in the ortho- or meta-

position increases the rate of decomposition, whereas one in the para-position exerts the normal inhibiting influence.

The values of the velocity-coefficient K at 50° for the decomposition into phenols and nitrogen of a series of diazonium chlorides are given in the table :

Benzene.........	0·027	*o*-Anisole	0·000011
o-Toluene	0·077	*p*-Anisole	0·000012
m-Toluene......	0·08	*o*-Chlorobenzene	0·0000068
p-Toluene	0·0018	*m*-Chlorobenzene	0·00115
ψ-Cumene	0·068	*p*-Chlorobenzene	0·00015
m-Benzoic acid	0·0264	*m*-Bromobenzene	0·0030
p-Benzoic acid	0·0059	*p*-Bromobenzene	0·00027

m-*Carboxybenzenediazonium chloride*, $CO_2H\cdot C_6H_4\cdot NCl\vdots N$, is prepared by the action of amyl nitrite on an alcoholic solution of the hydrochloride of *m*-aminobenzoic acid, and forms yellowish-white crystals, exploding at 105°, but melting at 149—150° when carefully heated. The corresponding *derivative* of *p*-benzoic acid forms slender, white needles; o-*anisolediazonium chloride* could not be obtained in a crystalline condition. K. J. P. O.

Equilibrium of the Isomeric Forms of Diazoamino-compounds. Wilhelm Vaubel (*Zeit. angew. Chem.*, 1902, **15**, 1209—1211. Compare Abstr., 1900, i, 615).—Diazoamino-compounds exist generally in two forms; the primary form is labile and readily passes into a stable secondary form; the reverse process has not yet been observed. In the decomposition of both forms by hydrochloric acid, the amino-group always remains attached to the benzene nucleus, which contains electro-negative groups. When a diazoamino compound is acted on by bromine, simultaneous bromination and decomposition occurs; in this case, also, the amino-group is combined with the nucleus which has been attacked by the bromine. K. J. P. O.

Action of Alkali-hydroxides on *o*-Aziminobenzoic Acid. Eugen Bamberger and Ed. Demuth (*Ber.*, 1903, **36**, 374—376).—*o*-Aziminobenzoic acid is converted by boiling $2N$-sodium hydroxide solution into *o*-azoxybenzoic acid, $ON_2(C_6H_8\cdot CO_2H)_2$, and anthranilic acid. T. M. L.

Physical Changes in the Condition of Colloids. II. Behaviour of Proteids towards Electrolytes. Wolfgang Pauli (*Beitr. chem. Physiol. Path.*, 1902, **3**, 225—246. Compare Abstr., 1902, ii, 388).—Salts effect changes of two kinds in the state of organic colloids, a superficial reversible, possibly chemical, change and a deep-seated chemical change. The former is the case in the precipitation of proteids by neutral alkali and magnesium salts, and the latter in the precipitations by the salts of heavy metals. Hofmeister's method of salting out proteids is an application of the reaction of the first type. An account of an exhaustive series of experiments with a great number of neutral salts of alkali metals and magnesium is given in the paper.

It is shown that the precipitating power of a salt depends both on the cathion and the anion, and that the action of the cathion and the anion in a given salt are mutually independent of one another. The precipitating power of a given electrolyte is accordingly an additive function of the two ions. Certain salts are, however, an exception to this rule; they do not precipitate proteids, although the ions present in them are capable, when present in other electrolytes, of producing precipitation. For example, potassium and sodium salts resemble one another very closely as regards this property, yet, compared to sodium sulphate, potassium sulphate has little precipitating power. K. J. P. O.

Iodised Decomposition Products of Proteids. Adolf Oswald (*Beitr. chem. Physiol. Path.*, 1903, 3, 391—416. Compare Abstr., 1901, ii, 461; 1902, ii, 677).—Albumoses and peptone were separated by Pick's method from Witte's peptone, and were iodised by either Kuraéeff's or Blum and Vaubel's method. An elementary analysis of each was then made; the percentage of iodine in the different products varied from 10·27 to 14·67. Iodohetero-albumose contains the smallest amount of iodine. Evidence is adduced to show that the iodine is chiefly, but not exclusively, united to the tyrosine radicle. W. D. H.

Acid Properties and Molecular Weight of Casein and its Decomposition on Drying. E. Laqueur and Otto Sackur (*Beitr. chem. Physiol. Path.*, 1902, 3, 193—224).—Determinations of the solubility of casein in water at 18° show that it has no measurable solubility. From its power of neutralising bases in the presence of phenolphthalein, the equivalent weight appears to be 1135 (compare Spiro and Pemsel, Abstr., 1899, ii, 230; and Osborne, Abstr., 1902, i, 194). From the change of the electrical conductivity of casein salts with dilution, it is estimated that casein is either a tetra- or hexabasic acid. That the casein salts are hydrolysed follows from the optical properties of the solution and from the fact that the neutral point is independent of the indicator, and that the degree of viscosity of solutions of casein salts is greatly dependent on the presence of small quantities of acids and alkalis. The viscosity of casein salt solutions is mainly conditioned by the concentration of the casein ions.

When dried at 100°, casein is changed in such a manner that on subsequent treatment with dilute sodium hydroxide, it yields an insoluble substance (sodium caseide) and a readily soluble substance, *iso*casein. The former substance is an alkali-albuminate which shows all the reactions of casein; the latter substance is a new proteid having the same mol. weight as casein. It contains more nitrogen (15·8 per cent.) than casein (15·45—15·48 per cent.), and, using Hofmeister's standard (Abstr., 1898, ii, 615), is precipitated by 4 cm. ammonium sulphate, whereas casein is precipitated by 3·4—3·6 cm. It gives the ordinary proteid reactions with the exception of the lead acetate test; its salts are less hydrolysed than those of casein in aqueous solution,

as is shown by the greater viscosity of the solutions, and have a greater equivalent conductivity. Rennet clears the solution only very slowly and incompletely. The casein of human and goats' milk behaves in the same way when dried. K. J. P. O.

Decomposition of Gelatin. I. Amounts of Glycine from Gelatoses. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1902, 37, 81—85).—Gelatin and various gelatoses have been hydrolysed by boiling with hydrochloric acid of sp. gr. 1·20 for 6 hours, and the amounts of glycine estimated by E. Fischer's method (Abstr., 1902, i, 512). The other products present do not interfere with the separation of the hydrochloride of ethylglycine. The amounts obtained were gelatin (dried at 120°), 16·43; gelatin, purified by Chittenden's method, 16·34; proto-peptogelatose, 18·36; proto-trypogelatose, 17·07; proto-papaiogelatose, 20·29; deutero-peptogelatose, 19·96; deutero-tryptogelatose, 20·29; and deutero-papaiogelatose, 19·33 per cent. J. J. S.

Physiological Relations of Derivatives of Proteids containing Sulphur. II. α-Thiolactic Acid, a Decomposition Product of Keratin-substance. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1902, 3, 184—192. Compare this vol., i, 75).—Suter (Abstr., 1895, ii, 691) found α-thiolactic acid in the product of hydrolysis of horn which had putrefied, and was of the opinion that it was not a primary product, but arose in the putrefaction. Horn parings (1 kilo.) were hydrolysed with fuming hydrochloric acid (3 litres), and the product exactly neutralised with concentrated sodium hydroxide, and then mixed with mercuric acetate (300 grams) The precipitate (I), when freed from mercury by means of hydrogen sulphide, gave only cystein; a further addition of sodium hydroxide produced a precipitate (II), which also contained only cystein. If now mercuric acetate (400 grams) is added to this strongly alkaline solution, a precipitate is thrown down, from which, after treatment with hydrogen sulphide, α-thiolactic acid can be isolated in the form of its benzyl derivative (compare Suter, *loc. cit.*). By the same method, α-thiolactic acid was obtained by the hydrolysis of keratin and goose feathers. From wool and human hair, the disulphide of α-thiolactic acid is obtained; at the same time, from the liquid which has been precipitated with mercuric acetate a substance can be extracted with ether which gives a deep red coloration with ferric chloride and ammonia, and is probably thioglycollic acid.

Since pure α-thiolactic acid can be precipitated with mercuric acetate, whereas the acid can only be obtained from the product of the hydrolysis of horn after the addition of alkali, it is possible that the acid is only formed as a secondary product from other substances containing sulphur. It is, however, not formed by the action of hydrogen sulphide on pyruvic acid, as this acid is not produced in the hydrolysis of horn. K. J. P. O.

The Lecithans and their Function in the Life of the Cell. WALDEMAR KOCH (*Dec. Pub. Univ. Chicago*, 1902, 10, reprint, 12 pp.; *Zeit. physiol. Chem.*, 1903, 37, 181—188).—The author classifies under the term "lecithans" those substances, such as egg lecithin, brain lecithin, kephalin, myelin, and paramyelin, which contain in the mole-

cule, phosphoric acid, fatty acids, nitrogen, and, in most cases, glycerol. They are waxy, non-crystalline, hygroscopic substances.

Brain lecithin, when immersed in water, swells up and projects long filaments (myelins), and, after some time forms a perfect emulsion. Salts of univalent and tervalent cathions do not cause a precipitation of the emulsion, but salts of bivalent cathions and acids produce a flocculent precipitate which settles well. Non-electrolytes, such as albumin, peptones, dextrose, carbamide, alkaloids, urethanes, and chloral, do not cause precipitation, nor do any of the anions examined. The precipitation by hydrogen ions or bivalent cathions is independent of the concentration of the lecithin, and the precipitate is redissolved by pure water. The addition of a small quantity of a sodium salt prevents the precipitation by a calcium salt, but non-electrolytes do not hinder the precipitation.

The chemical properties of the lecithans depend on two groups present in the molecule : (1) the fatty acids, and (2) the complex containing the nitrogen. All lecithans contain two fatty acids ; one of these is palmitic, stearic, or margaric acid, and does not impart any particular property to the compound ; the other is an unsaturated acid, oleic in the case of lecithan, and kephalinic in the case of kephalin, and gives to the molecule its distinctive character.

The number of methyl groups attached to nitrogen in some of these lecithans was determined by the method of Herzig and Meyer. Kephalin contains one methyl group per atom of nitrogen, whilst brain lecithin contains three methyl groups. The lecithan from yeast contains more than one methyl group per atom of nitrogen, and the excess is attributed to the presence of some lecithin ; the main part, however, appears to be kephalin.

It is noteworthy that kephalin is only found in living cells, such as the nerve cell or yeast cell, and is not present in the egg, which consists of stored food material. Kephalin does not contain a neurin molecule, and perhaps it is an intermediary product in the decomposition of lecithin. J. McC.

Glycocholeic Acid. V. WAHLGREN (*Zeit. physiol. Chem.*, 1902, **36**, 556—567).—From ox-gall, a new acid has been obtained by the following process : the bile is evaporated to a syrup and the residue extracted with alcohol ; the solution is evaporated to dryness, the residue dissolved in water and precipitated with lead acetate ; the lead salt is converted into the sodium salt by the action of sodium carbonate and the latter in the dry state extracted with alcohol, which leaves a part undissolved ; this part is dissolved in water and precipitated as barium salt with barium chloride ; from this salt, the free acid is obtained by treatment with hydrochloric acid, and may be again further purified by conversion into the sodium or barium salts. *Glycocholeic acid*, $C_{27}H_{45}O_5N$ or $C_{26}H_{43}O_5N$ (accordingly as the choleic acid present in the substance is represented by Latschinoff's or Lassar-Cohn's formula), crystallises in thick prisms melting at 175—176°, is little soluble in water, has a bitter taste, and gives Pettenkofer's test. Its alkali salts are precipitated by the alkaline earths and also by neutral salts such as sodium chloride, acetate, and sulphate ; in this respect, it differs

from glycocholic acid. When hydrolysed by barium hydroxide or hydrochloric acid, it yields glycine and choleic acid, the latter being probably identical with Latschinoff's acid (Abstr., 1886, 718). Glycocholeic acid is probably identical with Mulder's cholonic acid (*Annalen*, 1849, 70), but different from Strecker's acid (*Annalen*, 1848, 65) of the same name. The latter is formed by boiling glycocholic acid with water, and might therefore be called paraglycocholic acid.

K. J. P. O.

Protamines. M. Goto (*Zeit. physiol. Chem.*, 1902, 37, 94—114. Compare Piccard, *Ber.*, 1874, 7, 1714; Cloetta, *Arch. Exp. Path. Pharm.*, 37; Kossel, Abstr., 1896, i, 582; 1898, i, 714).—The following protamines have been obtained from the testicles of different fish, namely, salmine from salmon, clupeine from herring, scombrine, and sturine. The platinichlorides were prepared by the addition of a methyl-alcoholic solution of platinic chloride to a solution of the hydrochloride of the base in the same solvent. The following formulæ agree best with the results of analysis: salmine platinichloride, $C_{30}H_{57}O_6N_{17},2H_2PtCl_6$, clupeine platinichloride, $C_{30}H_{62}O_9N_{14},2H_2PtCl_6$. The two bases do not appear to be identical, as suggested by Kossel. Scombrine platinichloride, $C_{32}H_{72}O_8N_{16},2H_2PtCl_6$. Sturine platinichloride, $C_{34}H_{71}O_9N_{17},2H_2PtCl_6$.

The protamines have been transformed into protones by boiling with dilute sulphuric acid for half an hour. The protones are not precipitated by ammonia, but give an intense biuret reaction. They yield precipitates with sodium picrate, sodium tungstate, potassium ferrocyanide, potassium iodide, auric chloride, platinic chloride, and mercuric chloride. Saturated sodium chloride solution produces no precipitate, and solutions of protones do not give the Molisch and Hopkins reactions. Clupeone readily dissolves cupric oxide, yielding a violet compound containing 11·62 per cent. of copper. Clupeine gives a similar derivative containing 9·23 per cent. of copper. Clupeone has a molecular weight of about 420. The protones and their sulphates are all lævorotatory in solution. Cluepeone has $[\alpha]_D$ −22·02; the sulphate, $[\alpha]_D$ −49·11; scombrone sulphate, $[\alpha]_D$ −41·25; and sturone sulphate, $[\alpha]_D$ −22·5.

The results of analysis point to the following formula for *clupeone platinichloride*, $C_{28}H_{56}O_8N_{14},2H_2PtCl_6$. Clupeone appears to contain as much arginine as clupeine itself, 80 per cent. of the total nitrogen being present as arginine.

Hydrochloric acid produces ammonia from clupeine, but sulphuric does not.

J. J. S.

A Basic Constituent of the Animal Cell. Albrecht Kossel and H. Steudel (*Zeit. physiol. Chem.*, 1902, 37, 177—180).—Cytosine, obtained from the testicle of the sturgeon, has the molecular formula $C_4H_5ON_3$ and crystallises with $1H_2O$. It is not very readily soluble in water, but yields a soluble sulphate and hydrochloride and a sparingly soluble picrate and *platinichloride*, $(C_4H_5ON_3)_2,H_2PtCl_6$. Its connection, or perhaps identity, with thymus cytosine has not yet been established.

J. J. S.

Blue Colouring Matter from the Fins of Crenilabrus pavo. Richard von Zeynek (*Zeit. physiol. Chem.*, 1902, 36, 568—574. Compare Abstr., 1902, i, 168).—In the breeding season, *Crenilabrus pavo* assumes a blue colour, due to the formation of a blue pigment, which can easily be obtained from the fins. The fins are first treated with ether and acetone, and the pigment then extracted with distilled water. The extract is freed from proteid by precipitation with ammonium sulphate, and after removing the salt by dialysis, the pigment is obtained by evaporation; it forms transparent, brittle lamellæ, the solubility of which in water gradually decreases on keeping. The dye is free from phosphorus, iron, and copper, and has the composition: C, 50·09; H, 6·82; N, 14·85; S, 0·62; and O, 27·62 per cent. It gives the usual proteid reactions, except that with Millon's reagent. Nitric acid causes a transient reddish-violet coloration. When the solution is boiled with hydrochloric acid, it is first decolorised and then becomes an intense indigo-blue colour, which shows the spectrum of indigo-carmine. Other *Crenilabri* seem to possess the same colouring matter, whilst *Labrus turdus* has a bluish-black pigment having different properties. K. J. P. O.

Nomenclature of Enzymes. Edmund O. von Lippmann (*Ber.*, 1903, 36, 331—332).—As considerable confusion exists in the nomenclature of enzymes, it is suggested that each enzyme should be denoted by a name composed of the name of the substance which is changed and the name of the substance which is formed; thus the enzyme which converts starch into maltose, should be called "amylo-maltase," and that which converts maltose into dextrose (glucose), "malto-glucase," &c. If a shorter name is preferred, then the syllable "ase" could be affixed to the product of the action of the ferment; thus "maltase" should denote an enzyme by the action of which maltose is produced.
K. J. P. O.

Law of Action of Invertase. Victor Henri (*Compt. rend. Soc. Biol.*, 1902, 54, 1215—1216).—The formula previously proposed (Abstr., 1901, i, 438) for the inversion of cane sugar by invertase, $K = 1/t.\log(a+x/a-x)$, where x is the amount of sugar inverted after t minutes, holds for the conversion of a given quantity of sugar, but the value of K changes when the original concentration of the sugar solution is altered; the formula, moreover, is purely empirical. A better result is obtained by a formula, suggested by Bodenstein, which is based on the assumption that the rate is diminished both by the sucrose itself and the products of inversion, so that the velocity becomes $K_2 \dfrac{F}{m(a-x)+nx}(a-x)$ (where F is the amount of ferment, $m=2$, and $n=1$). This formula gives results independent of the original concentration, provided that this is not too low, but fails entirely for very low concentrations. A. H.

Organic Chemistry.

Action of Hydrazine Hydrate on Ethylene Bromide. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 67, 143—144).—When hydrazine hydrate and ethylene bromide are heated together in sealed tubes, acetylene is not formed (compare v. Rothenburg, *Ber.*, 1893, 26, 865). The benzaldehyde compounds of three bases melting at 128°, 138°, and 208°, and having the compositions $C_{23}H_{22}N_4$, $C_{32}H_{32}N_6$, and $C_9H_{10}N_2$ respectively, have been isolated from the product. E. F. A.

Action of Water on Pentamethylene Bromide. ARMIN HOCHSTETTER (*Monatsh.*, 1902, 23, 1071—1074).—When heated with water at 100° under pressure, pentamethylene bromide (Gustavson and Demjanoff, Abstr., 1889, 950) is converted into pentamethylene oxide (Demjanoff, Abstr., 1892, 1292), which boils at 81—82° and does not react with zinc ethyl at 100°. G. Y.

Electrolytic Preparation of Iodoform from Acetone. HOWE ABBOTT (*J. Physical Chem.*, 1903, 84—91).—The most favourable conditions for this preparation are a current density of about 1·35 amperes per square decimetre, a temperature of 75° with an anode solution consisting of 6 grams of sodium carbonate, 10 grams of potassium iodide, 100 c.c. of water, and 5·5 c.c. of acetone added at the rate of 0·5 c.c. per 10 minutes during the electrolysis. The yield obtained from the acetone was about 47 per cent., and the iodoform formed was about 0·57 gram per watt hour. The author considers it most probable that tri-iodoacetone is first formed, which then undergoes hydrolysis with the formation of iodoform and acetic acid. L. M. J.

Constitution of the Primary Dinitro-hydrocarbons, $CHRN_2O_4$. GIACOMO PONZIO (*J. pr. Chem.*, 1903, [ii], 67, 137—139).—Water acts on the potassium derivatives of the dinitro-hydrocarbons to form ammonia, potassium nitrite and the potassium salt of the corresponding fatty acid. This and the facts discussed in earlier papers (compare Abstr., 1902, i, 334) prove that the so-called primary dinitro-hydrocarbons contain (1) a single NO_2 group ; (2) one atom of nitrogen united directly to carbon ; (3) an oxygen atom united to carbon, and (4) an oximido-radicle. They are thus probably nitro-hydroxamic acids of the type $NO_2{\cdot}O{\cdot}CR{:}N{\cdot}OH$. E. F. A.

Tetranitromethane. AMÉ PICTET and P. GENEQUAND (*Arch. Sci. phys. nat.*, 1903, [iv], 15, 234).—By gently warming molecular proportions of acetic anhydride and diacetylorthonitric acid (Abstr., 1902, i, 584), tetranitromethane is formed, nitrous fumes and carbon dioxide being evolved. G. D. L.

Decomposition of Ethyl Alcohol at High Temperatures with Carbon, Aluminium, and Magnesium. By RICHARD EHRENFELD (*J. pr. Chem.*, 1903, [ii], **67**, 49—93).—When the vapour of ethyl alcohol is passed over carbon heated to dull redness, it is decomposed into equal volumes of methane, carbon monoxide and hydrogen, according to the equation $C_2H_6O = CH_4 + CO + H_2$.

At a lower temperature, large quantities of ethane are formed, probably as a primary reduction product. The possible secondary formation of ethane from primary decomposition products is disproved by the absence of aliphatic or cyclic polymerisation products and of substances which, under the influence of water, could give ethane.

When distilled over aluminium below a dull red heat, the products are ethylene and water, the latter being, to a large extent, further reduced to hydrogen. At a dull red heat, decomposition into methane, carbon monoxide and hydrogen also takes place, and, at a bright red heat, is predominant. At a yellow heat, an energetic reduction of the carbon monoxide takes place, but the decomposition into ethylene and water still accompanies that which gives methane, carbon monoxide and hydrogen.

When distilled over magnesium, a similar series of decomposition products is obtained, although relatively much more hydrogen is produced.

In general, whilst alcohol decomposes in two modes, the relative proportion of these is influenced more largely by the specific nature of the substance over which it is distilled than by changes in temperature. E. F. A.

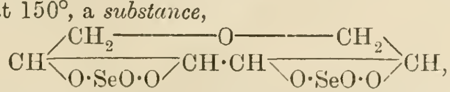
Preparation and Properties of Hexane-$\alpha\zeta$-diol, or Hexamethylene glycol, and its Principal Derivatives. JULES HAMONET (*Compt. rend.*, 1903, **136**, 244—246).—Hexamethylene glycol was obtained from diphenoxyhexane (this vol., i, 251) by converting the latter successively into di-iodohexane and hexanediol diacetate, which was then hydrolysed. $\alpha\zeta$-Di-iodohexane, prepared by heating diphenoxyhexane with concentrated hydriodic acid under pressure at 120°, crystallises in colourless needles melting at 9·5°, boiling at 163° under 17·5 mm. pressure, and having a sp. gr. 2·5 at 18°; Salonina (Abstr., 1894, i, 119) found that this substance melted at −7°. *Hexanediol diacetate*, prepared by the action of silver acetate on the iodide, crystallises in colourless needles melting at 5° and boiling at 142° under 16 mm., and at 262° under 765 mm. pressure; it has a sp. gr. 1·017 at 18°. Hexamethylene $\alpha\zeta$-glycol, $OH\cdot CH_2\cdot[CH_2]_4\cdot CH_2(OH)$, prepared from the last-mentioned compound by heating it on the water-bath with powdered potassium hydroxide, crystallises in needles melting at 42° and boiling at 152° under 17 mm., and at 254° under 767 mm. pressure; this substance does not resemble the hexamethylene glycol obtained by Haworth and Perkin (Trans., 1898, **73**, 330), who describe it as a syrup boiling and decomposing at 235—240°. *Hexamethylene dibenzoate*, prepared from the iodide and silver benzoate, crystallises in leaflets melting at 56°; the *dicarbanil* derivative, $C_6H_{12}(O\cdot CO\cdot NHPh)_2$, prepared from the glycol and phenylcarbimide, forms crystals melting at 171—172°. *Dicyanohexane* (suberonitrile), $C_6H_{12}(CN)_2$, is a colour-

less liquid, which boils at 185° under 15 mm. pressure, has a sp. gr. 0·954 at 18°, and solidifies, forming needles melting at $-3·5°$; when heated under pressure with hydrochloric acid, it is converted into suberic acid (m. p. 140°). K. J. P. O.

Action of Phosphoric Acid on Erythritol. P. CARRÉ (*Compt. rend.*, 1903, 136, 456—467. Compare following abstract).—Phosphoric acid exerts a dehydrating action on erythritol. When molecular quantities of these two substances are heated at 125°, only one of the hydroxyl groups of the phosphoric acid is esterified. By more prolonged heating, a second hydroxyl group is esterified, but the third hydroxyl group cannot be. After heating for 100 hours, 44·4 per cent. of the phosphoric acid was in the form of dierythritol ester, and 19·8 per cent. in the form of monoerythritol ester. The mono-ester has been isolated in the form of its *barium* salt, $BaPO_3(O·C_4H_7O_2),H_2O$. This is easily soluble in water, and loses its water of crystallisation at 140—150°. The *lead* salt is insoluble in water. It has not been possible either to isolate the mono-ester in the pure state, or to separate the di-ester. J. McC.

Esterification of Mannitol by Phosphoric Acid. P. CARRÉ (*Compt. rend.*, 1903, 136, 306—308).—Portes and Prunier (Abstr., 1902, i, 526) have obtained an acid phosphate of mannitol by heating together mannitol and phosphoric acid. It is found that when the experiments are carried out by the method used by these chemists, dehydration of the mannitol takes place, and consequently the ester has not the formula $PO(OH)_2·O·C_6H_{13}O_5$; if a 50 per cent. solution of mannitol and a 62 per cent. solution of phosphoric acid are heated together at 125° under reduced pressure (20 mm.), a much larger yield of the ester is obtained. In both cases, a mixture of two esters is produced, the one, $PO(OH)_2·O·C_6H_9O_3$, identical with that prepared by Portes and Prunier, is formed in much larger quantity, and is monobasic to methyl-orange and dibasic to phenolphthalein; the other, $PO(OH)(OR)_2$, is monobasic to phenolphthalein and was not isolated. The barium salt, $BaO_2·PO·O·C_6H_9O_3,H_2O$, was prepared; it loses water at 140—150°. On attempting to isolate the acid from the barium salt, decomposition takes place. K. J. P. O.

Action of Selenyl Chloride on Mannitol. CAMILLE CHABRIÉ and A. BOUCHONNET (*Compt. rend.*, 1903, 136, 376—377).—In continuation of the study of the action of selenyl chloride on polyhydric alcohols (compare Abstr., 1902, i, 657), the behaviour of mannitol with this substance has been investigated. When mannitol (1 mol.) and selenyl chloride (2 mols.) are heated at 120—130° for two hours, a yellow oil of the consistence of collodium is formed, which is soluble in water. If the residue left on evaporating the aqueous solution is again heated at 150°, a *substance*,



is obtained, which crystallises in long, very hygroscopic needles soften

ing at 90°, changing at 150°, and decomposing very rapidly at 190°. The whole of the selenium is precipitated from the hot aqueous solution by sulphur dioxide. K. J. P. O.

Ammonium Salts. Richard Reik (*Monatsh.*, 1902, **23**, 1033—1070).—When recrystallised from hot formic acid or when distilled under the atmospheric pressure, ammonium formate does not yield an acid salt. When perfectly dry, ammonium formate sublimes unchanged at 145° and under 8—20 mm. pressure; if the pressure rises to 25 mm., the salt melts and distils with slight decomposition if traces of moisture are present.

Normal ammonium acetate, prepared by passing ammonia into anhydrous acetic acid dissolved in ether, melts at 112·5—114° (compare Kraut, *Arch. Pharm.*, 1863, **116**, 38). When sublimed or distilled under reduced pressure, ammonium acetate undergoes partial decomposition, yielding mixtures of the normal and acid salts. Commercial ammonium acetate also contains these salts, and there are no grounds for considering it to have a definite composition (compare Berthelot, *Bull. Soc. chim.*, 1875, **24**, 107).

Ammonium hydrogen acetate, $NH_4C_2H_3O_2,C_2H_4O_2$, cannot be prepared by distilling ammonium acetate or by keeping ammonium acetate over sulphuric acid (Kraut), but is obtained when the normal salt is recrystallised from glacial acetic acid (compare Berthelot, *loc. cit.*). When treated with hot glacial acetic acid, the hydrogen acetate is partly reconverted into the normal salt. Ammonium hydrogen acetate melts at 66—66·5°, is soluble in alcohol, and can be sublimed or distilled under reduced pressure. The aqueous solution has a strongly acid reaction. On addition of ether to the alcoholic solution of the hydrogen acetate, a precipitate is formed consisting principally of the normal acetate. An ammonium dihydrogen acetate could not be formed.

Ammonium propionate loses ammonia when kept in a vacuum; when distilled, it yields ammonium hydrogen propionate (Sestini, *Zeit. Chem.*, 1871, **14**, 35). When distilled, ammonium *iso*valerate yields the hydrogen valerate, but under reduced pressure principally the diacid salt, $NH_4C_5H_9O_2,2C_5H_{10}O_2$.

At 210° and under 11 mm. pressure, ammonium nitrate distils unchanged.

Smith's statement (Abstr., 1894, ii, 13) that ammonium sulphate does not melt, but when heated evolves ammonia and is converted into ammonium hydrogen sulphate, is confirmed.

By means of a new form of apparatus, the author has determined the vapour pressure of ammonium hydrogen acetate for temperatures between 67° and 100°, and the sublimation point of ammonium formate for pressures between 10·5 and 24·5 mm. Vapour density determinations by Bleier and Kohn's method (Abstr., 1899, ii, 643) show ammonium hydrogen acetate and formate to be fully dissociated in the state of vapour. This may, however, be due to the presence of moisture (Baker, Trans., 1894, **65**, 611).

Acid salts of the fatty acids, such as ammonium hydrogen acetate,

must be regarded as simple molecules and not as molecular combinations. G. Y.

Oxidation of the Acetates of Cobalt and Manganese by Chlorine. H. Copaux (*Compt. rend.*, 1903, **136**, 373—375. Compare Abstr., 1902, i, 586).—When chlorine is led into the red solution of cobaltous acetate, it becomes green, and, on slowly evaporating the water, the *compound*, $4Co_3(OAc)_4,CoCl_2,40H_2O$, separates in leaflets which are green, but appear black by reflected light. This substance may be prepared by adding cobaltous acetate (1 part) to 5 per cent. acetic acid (2 parts), and simultaneously passing in chlorine; or by oxidising a solution of cobaltous acetate by the electric current, evaporating to dryness, when an amorphous green powder is obtained, and dissolving the residue in dilute acetic acid and adding cobalt chloride. The aqueous solution of this compound is green and neutral in reaction; it gives a precipitate of silver chloride with silver nitrate, and a precipitate with large excess of potassium hydroxide. On boiling the solution, it becomes brown and acetic acid vapour is evolved; on adding ammonium sulphate to the brown solution, a precipitate is formed. This compound is regarded not as the acetate of the oxide, Co_3O_4, but as a derivative of cobaltocobaltiacetate, analogous to the cobaltocobalticyanides (compare Jackson and Comey, Abstr., 1897, i, 390).

Highly concentrated acid solutions of manganous acetate (40 per cent.) are converted into manganic acetate by the action of chlorine. A 15 per cent. solution of manganous acetate is oxidised, manganese manganite (Gorgeu) being precipitated. K. J. P. O.

Preparation of the Anhydrides of Fatty Acids. Henri Kessler (D.R.-P. 132605).—The use of sulphur chloride in the preparation of acetic anhydride is, under ordinary conditions, impracticable, owing to contamination of the product with sulphur compounds. By heating dry sodium acetate (or the sodium salts of higher fatty acids) with sulphur chloride containing the theoretical quantity of SCl_2 under reduced pressure and distilling in a vacuum, a very pure product is formed. The same cast iron vessel can be used for the whole operation, and at the low temperature of the reaction no sulphur compounds distil over. C. H. D.

Mixed Anhydrides of Mineral and Organic Acids. Amé Pictet, A. Geleznoff, and H. Friedmann (*Arch. Sci. phys. nat.*, 1903, [iv], **15**, 233).—Sulphuric and phosphoric oxides react with glacial acetic acid giving *acetic sulphuric anhydride*, $OH\cdot SO_2\cdot OAc$, and *diacetic pyrophosphoric anhydride*, $O[PO(OH)\cdot OAc]_2$, respectively. When acetic anhydride acts on boric acid, *triacetic boric anhydride*, $B(OAc)_3$, a crystalline solid melting at 130°, is obtained, and not, as formerly supposed, diacetylboric acid; it is readily acted on by water, giving boric and acetic acids, whilst alcohols form the corresponding esters; ammonia gives acetamide and ammonium borate, and phenol and α-naphthol yield their normal borates. G. D. L.

The Fatty Oil of Lemon Pips, and Limonin. W. Peters and Gustav Frerichs (*Arch. Pharm.*, 1902, **240**, 659—662).—From

the ground pips, light petroleum extracted an *oil* of sp. gr. 0·9 at 15°; iodine number, 109·2; saponification number, 188·35; acetyl-acid number, 195·8; and acetyl number, 13·65. The oil was found to contain the glyceryl esters of oleic, linoleic, palmitic, stearic, linolenic, and *iso*-linolenic acids.

From the residual meal, alcohol extracted limonin. Little that is new could be ascertained regarding this substance; analysis and the molecular weight determination agreed with the formula $C_{22}H_{26}O_7$; it seems to contain neither methoxyl nor hydroxyl groups, and the ordinary reagents have no action on it. It can be obtained from the pips of sweet and bitter oranges, as well as from those of lemons.

C. F. B.

Thio-acids, R·CO·SH. VICTOR AUGER and M. BILLY (*Compt. rend.*, 1903, **136**, 555—557).—In order to prepare acids of the type R·CO·SH, the action of sodium hydrosulphide on the phenyl esters, the alkyl esters, the amides and the thioamides, the acetyl derivatives of oximes and the acetyl derivatives of phenylhydrazine has been studied. Kekulé first prepared the thio-acids from the phenyl esters, and, by this method, several new acids have been prepared; *thiolmyristic acid*, $C_{13}H_{27}$·CO·SH, prepared by boiling the phenyl ester with alcoholic sodium hydrosulphide, crystallises in needles melting at 25°. *Thiolpalmitic acid*, $C_{15}H_{31}$·CO·SH, crystallises in needles melting at 71°. As has been previously shown, dibasic thio-acids such as thiosuccinic acid could not be prepared. *Sodium dithioloxalate*, $C_2O_2(SNa)_2$, can, however, be prepared from phenyl oxalate, and forms a crystalline, hygroscopic, yellow powder, and gives a series of coloured precipitates with the aqueous metallic salts; on acidifying the solution of this salt, an unstable, yellow solution is obtained, from which yellow flocks containing sulphur separate; they dissolve in alkali hydroxides with a blue-green coloration, which slowly fades when kept in the air.

Dithiolmalonic acid, as the *sodium* salt, CH_2(CO·SNa)$_2$, is prepared from phenyl malonate, which was obtained by treating a mixture of malonic acid and phenol with phosphorus oxychloride at the temperature of the water-bath (compare Bischoff and von Hedenström, this vol., i, 26, 27); the sodium salt crystallises in flattened needles.

The hydrolysis of ethereal salts of fatty alcohol radicles by means of sodium hydrosulphide has been investigated by Wanklyn (this Journal, 1864, **17**, 418) and Göttig (Abstr., 1886, 332); in the entire absence of water, no interaction between the hydrosulphide and the ester takes place below 180°, and at this temperature the mercaptan corresponding with the alcohol is alone formed.

Experiments with amides and thioamides show that even at 200° they are not hydrolysed, but that hydrogen sulphide is evolved and the sodium salt of the amide formed.

The acetyl derivatives of oximes, as instanced by benzaldoxime acetate, readily react with sodium hydrosulphide, yielding thioamides; thus, in the case of the example given, thiobenzamide is produced. The acetyl derivative of the oxime of acetophenone behaves in a peculiar manner, giving the oxime and ethyl acetate.

The mono- and di-acetyl derivatives of phenylhydrazine are not decomposed by sodium hydrosulphide, even at 220°. K. J. P. O.

Esters of Ricinoleic Acid. PAUL WALDEN (*Ber.*, 1903, 36, 781—790. Compare Abstr., 1895, i, 125, and H. Meyer, Abstr., 1898, i, 237).—The esters have been obtained by mixing the acid with an equal weight of the alcohol and saturating with hydrogen chloride, and have been purified by diluting with chloroform, washing with water, drying, and distilling. They are colourless or pale yellow liquids, lighter than water, and may be distilled under greatly reduced pressure. They are all optically active and dextrorotatory.

The following are the more important data:

Ester.	B. p.	Sp. gr.	n.	[α] red.	$[\alpha]_D$.	[α] blue.	[α] violet.
Methyl ...	245°, 10 mm.	0·9236 at 22°	1·4588	+3·8	5·05	7·24	9·64
Ethyl......	258°, 13 mm.	0·9145	1·4618	+4·07	5·28	7·87	9·01
*iso*Propyl .	260°, 10 mm.	0·9083	1·4583	+3·11	4·04	5·91	6·95
n-Propyl ..	268°, 13 mm.	0·9079	1·4573	+3·13	4·15	6·11	7·16
n-Butyl ...	275°, 13 mm.	0·9058	1·4566	+2·92	3·73	5·68	6·56
*iso*Butyl ..	262°, 9 mm.	0·9028	1·4538	+3·01	4·01	5·83	6·88
n-Heptyl .	295°, 10 mm.	0·8983	1·4566	+2·39	3·32	—	—

The molecular rotation tends to approximate to a constant value, namely, 20°, with an increase in mol. wt. of the ester. The dispersion coefficient is practically the same for all the esters, namely, 1·90 to 1·95. The molecular-rotation dispersion is, in most cases, approximately 10° at 22°, but sinks to about 4·5° at 100°.

Esters of acetylricinoleic acid:

Ester.	B. p.	Sp. gr.	n.	[α] red.	$[\alpha]_D$.	[α] blue.	[α] violet.
Methyl ...	260°, 13 mm.	0·9301	1·4570	+11·37	15·25	23·37	27·56
Ethyl ...	255—260°, 13 mm.	0·9170	1·4540	+11·19	14·85	23·22	27·62
n-Propyl .	about 260°, 13 mm.	0·9117	1·4513	+10·84	14·4	22·58	26·08
*iso*Butyl ..	255—260°, 13 mm.	0·9012	1·4548	+7·21	9·58	14·94	17·53

The molecular rotation for blue light tends to approximate to a constant value, about 85°, with increase in molecular weight. The dispersion coefficient $\frac{\text{blue}}{\text{red}}$ is approximately 2·05—2·08.

Esters of propionylricinoleic acid:

Ester.	B. p.	Sp. gr.	n.	[α] red.	$[\alpha]_D$.	[α] blue.	[α] violet.
Methyl ...	260°, 13 mm.	0·9226	1·4535	+12·82	16·88	26·35	30·37
Ethyl ...	265°, 13 mm.	0·9151	1·4517	+12·02	16·06	24·55	27·87
n-Propyl .	310—320°, 645 mm.	0·9128	1·4498	+10·32	13·61	—	—
*iso*Butyl ..	325—335°, 660 mm.	0·9027	1·4525	+6·91	9·2	14·31	16·3

The molecular rotations of the simple esters have also been determined in ethereal solution, and slightly higher values have been obtained. In all cases, increase of temperature diminishes the specific rotation; with the simple esters, the diminution is greater than with the acylated esters. J. J. S.

[Derivatives of Carboxylic Acids of the Acetylene Series.] CHARLES MOUREU (D.R.-P. 132802 and 133631. Compare Abstr., 1901, i, 361; 1902, i, 164, 253, 289).—Amylpropiolic acid is prepared by passing carbon dioxide into a solution of heptinene in dry ether or other solvent, to which 1 atom of sodium has been added for each molecule of the hydrocarbon, until the reaction is complete. Ice-water is then added, and, after acidifying, the acid is extracted with ether. Hexylpropiolic acid is similarly prepared from octinene.

The anilides, toluidides, and α-naphthalides of these acids find therapeutic application, and the esters are used in the preparation of perfumes.

On heating with alcoholic potash, the acids pass into the corresponding β-ketonic acids.

Amylpropiolic and hexylpropiolic acids may be esterified by heating with alcohols and sulphuric acid, or the sodium compounds of heptinene and octinene may be allowed to react with the esters of chlorocarbonic acid.

On treating the esters with sulphuric acid and pouring into water, the esters of the corresponding β-ketonic acids are formed.

C. H. D.

Some New Acids of the Acetylene Series. CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1903, **136**, 552—554. Compare Abstr., 1901, i, 359).—A number of acetylenic acids have been prepared by treatment of the sodium derivatives of substituted acetylenes, R·C⋮CNa, with carbon dioxide, or in the form of their ethyl esters by the use of ethyl chlorocarbonate. The substituted acetylenes were prepared from aldehydes or methyl ketones containing the same number of carbon atoms; in both cases, a dichloro-derivative was obtained from which 2 mols. of hydrogen chloride were withdrawn by treatment with alkali hydroxide; the dichloro-derivatives of the ketones yielded, besides the hydrocarbon of the type R·C⋮CH, the hydrocarbons R·C⋮CMe and $R\cdot CH{:}C{:}CH_2$, both of which are transformed by the action of sodium at 100° into the acetylene hydrocarbon of the type R·C⋮CH. The various hydrocarbons were not purified, but were directly converted into the sodium derivatives and then into the acids as above-mentioned.

Propylpropiolic [Δ_α-hexinoic] acid, $CPr^\alpha{⋮}C\cdot CO_2H$, forms crystals melting at 25° and boiling at 119—121° under 16 mm. and at 126—127° under 24 mm. pressure; the *methyl* ester boils at 80—82° under 23 mm. pressure and has a sp. gr. 0·9648 at 0°; the *ethyl* ester boils at 93—94° under 24 mm. pressure and has a sp. gr. 0·9468 at 0°; the *amyl* ester boils at 127—128° under 22 mm. pressure and has a sp. gr. 0·9207 at 0°.

*iso*Propylpropiolic acid [γ-methyl-Δ^α-pentinoic acid] melts at 36—38°

and boils at 114—115° under 18 mm. pressure; the *methyl* ester boils at 68—69° under 20 mm. pressure and has a sp. gr. 0·9509 at 0°; the *ethyl* ester boils at 83° under 19 mm. pressure and has a sp. gr. 0·9365 at 0°; the iso*butyl* ester boils at 99—101° under 19 mm. pressure and has a sp. gr. 0·9145 at 0°.

Butylpropiolic acid [Δ^{α}-heptinoic acid] boils at 140—142° under 24 mm. pressure; its *methyl* ester boils at 91—93° under 19 mm. pressure and has a sp. gr. 0·953 at 0°; the *ethyl* ester boils at 106—108° under 24 mm. pressure and has a sp. gr. 0·9385 at 0°. This and the two preceding acids have been previously prepared by Faworsky (Abstr., 1888, 1168).

Trimethyltetrolic acid [*$\gamma\gamma$-dimethyl-Δ^{α}-pentinoic acid*],

$CMe_3\cdot C⁝C\cdot CO_2H$,

melts at 47—48° and boils at 110° under 10 mm. pressure; its *methyl* ester boils at 66° under 13 mm. pressure and has a sp. gr. 0·9292 at 0°; the *ethyl* ester boils at 75° under 15 mm. pressure and has a sp. gr. 0·9209 at 0°.

iso*Amylpropiolic acid* [*ϵ-methyl-Δ^{α}-heptinoic acid*],

$CH_2Pr^{\beta}\cdot CH_2\cdot C⁝C\cdot CO_2H$,

melts at about 0°, boils at 141—144° under 19 mm. pressure, and has a sp. gr. 0·9647 at 18°; its *methyl* ester boils at 98—99° under 18 mm. pressure and has a sp. gr. 0·9417 at 0°; its *ethyl* ester boils at 110—112° under 18 mm. pressure and has a sp. gr. 0·9288 at 0°.

Hexylpropiolic acid [Δ^{α}-noninoic acid], which has been previously described (*loc. cit.*), forms an iso*propyl* ester boiling at 145—148° under 32 mm. pressure and having a sp. gr. 0·9101 at 0°; the iso*amyl* ester boils at 168—172° under 27 mm. pressure and has a sp. gr. 0·9074 at 0°; the *acid chloride* boils at 113—116° under 25 mm. pressure and has a sp. gr. 1·0007 at 0°; the *a-naphthylamide* melts at 99—100°.

iso*Hexylpropiolic acid* [*ζ-methyl-Δ_{α}-octinoic acid*] melts at – 16° to – 12°, boils at 169—172° under 20 mm. pressure, and has a sp. gr. 0·96 at 0°; the *methyl* ester boils at 125—127° under 31 mm. pressure and has a sp. gr. 0·933 at 0°; the *ethyl* ester boils at 135—137° under 30 mm. pressure and has a sp. gr. 0·922 at 0°.

Heptylpropiolic acid [*Δ^{α}-decinoic acid*] melts at 6—10°, boils at 164—168° under 20 mm. pressure, and has a sp. gr. 0·9408 at 17°; the *methyl* ester boils at 133—135° under 21 mm. pressure and has a sp. gr. 0·9263 at 0°; the *ethyl* ester boils at 143—146° under 21 mm. pressure and has a sp. gr. 0·9168 at 0°.

Nonylpropiolic acid [*Δ^{α}-undecinoic acid*] melts at 30°; its *methyl* ester boils at 68—72° under 31 mm. pressure and has a sp. gr. 0·9158 at 0°; the *ethyl* ester boils at 170—174° under 25 mm. pressure and has a sp. gr. 0·908 at 0°.

The following acids, which have both an acetylene and an ethylene linking, have been prepared. *δ-Methyl-Δ^{γ}-pentene-Δ^{α}-inoic acid,*

$CMe_2⁚CH\cdot C⁝C\cdot CO_2H$,

is prepared from the ketone, $CMe_2⁚CH\cdot COMe$, and melts at 98°. *ζ-Methyl-Δ^{ϵ}-octene-Δ^{α}-inoic acid,* $CMe_2⁚CH\cdot CH_2\cdot CH_2\cdot C⁝C\cdot CO_2H$, is prepared from the natural methylheptenone and boils at 157—159° under 20 mm. pressure and at 160—164° under 24 mm. pressure, and

has a sp. gr. 0·9906 at 0°; the *methyl* ester boils at 114—125° under 22 mm. pressure.

When distilled under the ordinary pressure, all these acids decompose into carbon dioxide and the acetylenic hydrocarbon; on reduction with sodium and absolute alcohol, the corresponding saturated fatty acid is obtained; thus a new *heptoic* acid, *trimethylbutyric acid* [*γ-methylvaleric acid*], $CMe_3\cdot CH_2\cdot CH_2\cdot CO_2H$, is prepared from trimethyltetrolic acid; it melts at $-1°$ to $+3°$, distils at 211—214° (corr.) under the ordinary pressure, and has a sp. gr. 0·914 at 20°; its *amide* melts at 140—141°. K. J. P. O.

Action of Carbamide on Pyruvic Acid. II. Dipyruvyl Triureide. LOUIS J. SIMON (*Compt. rend.*, 1903, 136, 506—508. Compare Abstr., 1902, i, 15).—Homoallantoic acid, or homoallantoin, dissolves in hydrochloric acid with production of dipyruvyltriureide; a better yield is, however, obtained by dissolving carbamide in concentrated hydrochloric acid and adding pyruvic acid. It forms white needles of the composition $C_9H_{12}O_5N_6,2H_2O$, which are sparingly soluble in water and insoluble in organic solvents. When rapidly heated, it decomposes at 350°; at 120—130°, it loses its water of crystallisation, and at 200° it undergoes no change. It dissolves in concentrated hydrochloric acid without alteration, but after some time hydrolysis takes place. It can be crystallised from water, but prolonged boiling causes decomposition into homoallantoin and a more condensed ureide. It is easily soluble in solutions of alkalis, and in these is more stable than in acid solution; on prolonged boiling, however, decomposition takes place, just as in aqueous solution. With silver nitrate solution, it precipitates a silver compound of the formula $C_9H_{12}O_5N_6,Ag_2O,3H_2O$, which is insoluble in water, unaffected by the action of light, and serves to distinguish between dipyruvyltriureide and homoallantoic acid and homoallantoin, which are not precipitable by silver salts. J. McC.

New Researches with Camphocarboxylic Acid. JULIUS W. BRÜHL (*Ber.*, 1903, 36, 668—673. Compare this vol., i, 4 and 64).—The old method of making camphocarboxylic acid by means of sodium is superior to the magnesium method proposed by Zelinsky (this vol., i, 229), as the yield is almost theoretical and the only by-product is borneol; the magnesium method gives only a 50 per cent. yield, and yields camphor, borneol, and other by-products, whilst the use of bromocamphor involves an additional process.

The coloration produced by the interaction of camphocarboxylic acid and ferric chloride depends largely on the conditions; a methyl-alcoholic solution of the acid gives a transient blue with a single drop of aqueous ferric chloride, and a transient green with an excess of the chloride; if, however, a solution of ferric chloride in methyl alcohol is used, the colours last several hours; ethyl-alcoholic solutions give similar, but less stable, tints; the colour of the alcoholic solutions is at once destroyed by adding water. Solutions of the methyl ester in methyl or ethyl alcohol give, with alcoholic ferric chloride, blue solutions, which are not decolorised by diluting with water; the methyl-

alcoholic solutions can be boiled after diluting, but the diluted ethyl-alcoholic solution is decolorised by boiling. All the blue alcoholic solutions give a transient red with sodium acetate. Solutions in benzene of the acid or esters give no colour with a solution of ferric chloride in benzene, but if the methyl ester be converted first into the enolic sodium salt the solution in benzene gives, with a solution of ferric chloride in benzene, a blue-violet solution, which, on evaporation, leaves a black, powdery *ferric* salt, which is soluble with a blue colour in light petroleum, ether, or alcohol, and also yields a stable blue solution in water. T. M. L.

$\alpha\beta$-Dimethylglutaric Acids. EDMOND E. BLAISE (*Compt. rend.*, 1903, **136**, 243—244).—The new dimethylglutaric acid obtained from ethyl bromopivalate (Abstr., 1902, i, 530) was possibly an $\alpha\beta$-dimethylglutaric acid; accordingly, the synthesis of the two stereoisomeric $\alpha\beta$-dimethylglutaric acids, from ethyl sodiocyanoacetate and ethyl tiglate and ethyl angelate respectively, has been attempted. The condensation of ethyl tiglate and cyanoacetate was carried out above the ordinary temperature, and led to the formation of an *ester*, $CO_2Et\cdot[CHMe]_2\cdot CH(CN)\cdot CO_2Et$, which boils at 172° under 17 mm. pressure. On hydrolysis, an acid is formed which loses carbon dioxide when heated at 145°, and does not yield an anhydride. In order to purify the dibasic acid thus obtained, it was converted into its ethyl ester, which boils at 138° under 24 mm. pressure; hydrolysis of the ester gave an *$\alpha\beta$-dimethylglutaric acid*, which melted at 82—88° and was converted immediately by acetyl chloride into an *anhydride* boiling at 273—276°. The *anilino*-acid, prepared by treating the anhydride with aniline, melts at 147°, and the p-*toluidino*-acid at 117—118° (compare Thorpe and Young, Trans., 1903, **83**, 357).

The condensation of ethyl angelate and cyanoacetate was effected in the cold in order to avoid the possibility of an isomeric change; the *cyano*-ester thus prepared boiled at 176° under 25 mm. pressure, and yields the same $\alpha\beta$-dimethylglutaric acid (m.p. 82—83°) as was obtained from ethyl tiglate. The dimethylglutaric acid obtained from ethyl bromopivalate, which melts at 74—75°, is, therefore, not identical with the $\alpha\beta$-dimethylglutaric acid, here described. K. J. P. O.

Preparation of some Compounds of α-Methyl-δ-*iso*propyladipic Acid. CAMILLE MARTINE (*Compt. rend.*, 1903, **136**, 458—459. Compare Abstr., 1902, i, 629).—The dimethyl and diethyl esters of α-methyl-δ-*iso*propyladipic acid (*loc. cit.*) were obtained from the acid and alcohol by means of hydrogen chloride. The *dimethyl ester* boils at 143—144° under 22 mm. pressure or with decomposition at 251° under the ordinary pressure. The *diethyl ester* boils at 158° under 19 mm. pressure. Equal quantities of the acid and phosphorus trichloride, when heated on the water-bath, give *α-methyl-δ-*iso*propyladipyl chloride*, $C_8H_{16}(COCl)_2$, as an oil which distils at 247—248° under 25 mm. pressure. This chloride is not very stable and on keeping becomes brown. *α-Methyl-δ-*iso*propyladipyldiamide*, $C_8H_{16}(CO\cdot NH_2)_2$, is formed when ammonia is passed into a dry benzene solution of the chloride; it crystallises in white needles, which are insoluble in ether but soluble in hot alcohol, and melts at 242°. When the acid is

heated with aniline, no anilide is formed, but when the acid chloride is added to an excess of aniline dissolved in benzene, *α-methyl-δ-isopropyladipyldianilide*, $C_8H_{16}(CO\cdot NHPh)_2$, is formed. It is insoluble in ether, but soluble in hot alcohol, and melts at 231°. The corresponding *di-p-toluidide* melts at 229°. J. McC.

Migration of the Methyl Group under the Influence of Hydriodic Acid. EDMOND E. BLAISE (*Compt. rend.*, 1903, **136**, 381—383).—Ethyl glutaconate was converted by Henrich (Abstr., 1899, i, 794) into a dimethylglutaconic acid melting at 123—133°, which he has recently reduced by hydriodic acid to a dimethylglutaric acid (m. p. 106—107°; Abstr., 1902, i, 422). As has been shown, the reaction in which the dimethylglutaconic acid is formed by Henrich's method is very complex; at low temperatures, however, ethyl dimethylglutaconate is readily obtained, and boils at 131° under 14 mm. pressure. From this ester, the pure dimethylglutaconic acid can be prepared; it melts at 134—135°. The *anhydride* is a liquid and reacts with aniline yielding an *anilino*-acid melting at 162°, and at the same time a neutral *substance* containing nitrogen, which melts at 190—191°. As the dimethylglutaconic acid gives, on oxidation by permanganate, oxalic and dimethylmalonic acids, it is probably represented by the formula $CO_2H\cdot CMe_2\cdot CH\colon CH\cdot CO_2H$; whether it is identical with the acid obtained by Perkin (Proc., 1902, **18**, 214), is not certain, but it is quite different from the symmetrical dimethylglutaconic acid (m. p. 145—146°).

On reducing the dimethylglutaconic acid here described with hydriodic acid and red phosphorus, *cis-αγ*-dimethylglutaric acid is produced and purified by conversion into the *anhydride*, which forms crystals melting at 93° and boiling at 265—272°; the pure acid melts at 126—127°. Henrich's dimethylglutaric acid (m. p. 106—107°; *loc. cit.*) is a mixture of the *cis*- and *trans*-acids.

It is demonstrated, therefore, that in the treatment with hydriodic acid and phosphorus a methyl group has wandered from the α- to the γ-position. K. J. P. O.

Lichesteric Acid [Lichenostearic Acid]. RICHARD BÖHME (*Arch. Pharm.*, 1903, **241**, 1—22. Compare Sinnhold, Abstr., 1899, i, 13; Hesse, Abstr., 1898, i, 534; 1901, i, 87).—The paper incorporates some unpublished results by Pedersen. Lichesteric acid (*lichenostearic acid*), $C_{19}H_{32}O_4$, was prepared from Iceland moss in yield varying from 0·125 to 0·27 per cent.; it melts at 124—125° and has $[\alpha]_D$ +29·3° in 0·9 per cent., +29·0° in 1·7 per cent., solution at 15°. When prepared according to Hesse's method, potassium hydrogen carbonate being used in isolating it, it melts at 113—115°, and its ammonium salt will not crystallise; probably this is the same acid in an impure state, and not a new substance.

When the acid is distilled under 40 mm. pressure, it loses carbon dioxide and leaves a substance, $C_{18}H_{32}O_2$, melting at 42°. This appears to be a *lactone*, for it is neutral in character, but dissolves slowly when it is boiled with 10 per cent. aqueous potassium hydroxide, and from the solution sulphuric acid precipitates a substance having the composition $C_{18}H_{34}O_3$, and the character of an acid; presumably it is a

hydroxy-acid, $C_{14}H_{27}\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO_2H$. This acid melts at 82—84° and appears identical with the lichesterylic acid obtained by Sinnhold by boiling lichesteric (lichenostearic) acid with aqueous potassium hydroxide; it is also formed when aqueous barium hydroxide or sodium carbonate is used instead of potassium hydroxide, and again when the lactone mentioned above is fused with potassium hydroxide. Probably Hesse's lichestrone was this substance, and his lichesterylic acid the same substance in an impure state.

Lichesterylic acid, although containing a hydroxyl group, does not form an acetyl derivative when it is heated with acetic anhydride at 100°; the product is an oil from which a few crystals melting at 55—57° separate, and is apparently an anhydride; the same substance is formed together with diphenylcarbamide on heating the acid with phenylcarbimide in benzene solution at 100°. The acid is not changed either by treatment with sulphuric acid, or by heating at 200° under 40 mm. pressure.

When lichesteric (lichenostearic) acid is heated with hydriodic acid and red phosphorus at 200°, carbon dioxide is evolved, and if the oily product is boiled with zinc dust and glacial acetic acid, a saturated *hydrocarbon*, probably $C_{18}H_{38}$, is obtained together with an iso*stearic acid*, $C_{17}H_{35}\cdot CO_2H$. This is the third isomeride discovered, and is distinguished as λ; it melts at 49·5—50·5° and boils at about 200° under 25 mm. pressure, and can be distilled under the ordinary pressure. The crystalline *sodium* salt and the amorphous *silver* and *barium* salts were analysed; also the acid *chloride*, which melts at 50°, and the *ethyl ester*, which was prepared from the chloride.

The compounds in question have no unsaturated character, and so it is probable either that their formulæ should contain $C_{14}H_{29}$ instead of $C_{14}H_{27}$, or that they are cyclic compounds. C. F. B.

Condensation of Acetone with Ethyl Succinate. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 67, 197—199).—The *ester*,

$$O{<}\begin{matrix}CMe_2\cdot CH\cdot CO_2Et \\ CO{-\!-}C{:}CMe_2\end{matrix},$$

is obtained as a by-product in the preparation of ethyl teraconate by a modification of Stobbe's process (Abstr., 1894, i, 15). It crystallises from aqueous alcohol in glistening, six-sided scales, melts at 75°, boils at 165° under 12 mm. pressure, is easily soluble in alcohol or ether, and, on hydrolysis with alcoholic potassium hydroxide, yields the *potassium* salt, $CO_2K\cdot C({:}CMe_2)\cdot C({:}CMe_2)\cdot CO_2K$, which crystallises in glistening scales, and, with silver nitrate, forms the *silver* salt, $C_{10}H_{12}O_4Ag_2$. The *acid* melts and evolves gas at 231°, is easily soluble in alcohol or ether, cannot be reduced by sodium amalgam or sodium and alcohol to di*iso*propylsuccinic acid, and, on esterification, yields an *ethyl hydrogen* salt, which crystallises in leaflets and melts at 49°.

On esterification of teraconic acid, *ethyl hydrogen teraconate*,

$$CMe_2{:}C(CO_2H)\cdot CH_2\cdot CO_2Et,$$

is obtained which crystallises in delicate, colourless needles, melts at 118—120°, and is hydrolysed to teraconic acid on prolonged boiling with water. G. Y.

Isolation of Deoxycholic and Cholic Acids from Fresh Ox Bile and Oxidation Products of the Acids. FRITZ PREGL (*Monatsh.*, 1903, 24, 19—66).—The mother liquors obtained during the preparation of cholic acid (compare Lassar Cohn, Abstr., 1892, 741; and 1899, i, 552; and Mylius, Abstr., 1886, 490, 952; 1887, 606, 982; 1888, 508; and Vahlen, Abstr., 1896, 453) give, on treatment with alcohol containing ether, an abundant crystalline precipitate of deoxycholic acid, $C_{24}H_{40}O_4$. This, when pure, melts at 172—173°; when crystallised from alcohol containing ether, it contains a molecule of ether and melts at 153—155°; from acetic acid, it crystallises with a molecule of this acid and melts at 144—145°. When oxidised with chromic acid in the cold, dihydrocholeic acid is formed; whilst at higher temperatures, or by use of permanganate or nitric acid, cholanic acid, $C_{24}H_{36}O_7$, melting at 294—295°, is produced. Deoxycholic acid thus gives the same products when oxidised as Latschinoff's choleic acid (compare Abstr., 1887, 682, 683), and they are probably identical.

A simple method is described for preparing pure cholic acid from fresh ox bile and isolating this acid and deoxycholic acid from the mother liquors; by this means, it has been proved that there is at least 10 per cent. of deoxycholic acid in the so-called crude cholic acid. The normally insoluble barium salt of deoxycholic acid is kept in solution by barium cholate; this explains why barium chloride causes no precipitation from the crude mother liquors. Carboxyl estimations in the various fractions obtained have proved that below 10 per cent. CO_2H no crystallisation takes place, and thus the other substances present are probably not of an acid nature.

Bilianic acid, $C_{24}H_{34}O_8$, melting at 274—275°, is obtained on oxidising pure cholic acid with permanganate, together with cholanic acid from the crude cholic acid. With phosphorus pentachloride, it forms a crystalline compound, *dichloromonodeoxybilianic acid*, melting at 249—250°.

From cholic acid, both bilianic acid, melting at 274—275°, and *iso*bilianic acid, melting at 244—245°, are formed on oxidation. These differ in optical rotation and give different barium salts, but form apparently identical compounds with phenylhydrazine and hydroxylamine.

Cilianic acid, obtained by oxidation of bilianic acid, is shown to have the formula $C_{20}H_{28}O_8$, and not that given to it by Lassar Cohn (*loc. cit.*). In agreement with this, its trimethyl-ester has the composition $C_{20}H_{25}O_8Me_3$ and melts at 127—127·5°.

Cholic acid, on oxidation with permanganate, yields oxalic acid, and not phthalic acid as alleged by Senkowski (Abstr., 1896, 453).

E. F. A.

A New Synthesis effected by means of Molecules containing a Methylene Group attached to Two Negative Radicles. Action of Epichlorohydrin on the Sodium Derivative of Acetonedicarboxylic Esters. II. ALBIN HALLER and F. MARCH (*Compt. rend.*, 1903, 136, 434—436. Compare Abstr., 1901, i, 538).—Epichlorohydrin acts on the sodium derivative of ethyl acetone-

dicarboxylate in the same way as on the sodium derivatives of benzoyl acetic esters. The reaction is represented by the equation :

$$CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}CHNa{\cdot}CO_2Et + \begin{array}{l}O—\\ |\\ CH_2\end{array}\!\!>CH{\cdot}CH_2Cl =$$

$$CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}CH\!<\!\begin{array}{l}CO—O\\ CH_2{\cdot}CH\end{array}\!\!>CH_2Cl + EtONa.$$

The ethyl ester of the keto-lactonic acid was isolated in the form of its *copper* derivative, $Cu(C_{10}H_{12}O_5Cl)_2$, which melts at 224—225°, is insoluble in water, ether, or chloroform, but soluble in hot alcohol, and when decomposed with sulphuric acid and extracted with ether, yields the *ethyl* ester as a yellow oil which decomposes on heating. With semicarbazide hydrochloride in the presence of sodium acetate, it gives the *semicarbazone*, $C_{11}H_{16}O_5N_3Cl$, which forms white crystals, melts at 118—119°, and is insoluble in water, but easily soluble in hot alcohol or ether.

The same synthesis has been carried out with methyl acetonedicarboxylate and the *copper* derivative, $Cu(C_9H_{10}O_5Cl)_2$, obtained. This gave the *methyl* ester of the *keto-lactonic* acid, from which a *semicarbazone*, melting at 132—133°, was isolated. J. McC.

Esters of so-called Dinitrotartaric Acid. Paul Walden (*Ber.*, 1903, 36, 778—780. Compare Henry, *Ber.*, 1870, 3, 532; *Ann. Chim. phys.*, 1873, [iv], 28, 428; Walden, this vol., i, 148; Frankland, Heathcote, and Hartle, Trans., 1903, 83, 154).—The ester melting at 45—46° and first described by Henry as ethyl dinitrotartrate and then as ethyl nitrotartronate is in reality ethyl mononitrotartrate. All the compounds previously described by the author as esters of dinitrotartaric acids are really esters of the mononitro-acid.

J. J. S.

α- and β-2-Amino-*d*-glucoheptonic Acids. Carl Neuberg and Hans Wolff (*Ber.*, 1903, 36, 618—620).—In the preparation of a new α-hydroxy-β-aminoheptonic acid by the addition of hydrogen cyanide to glucosamine (chitosamine), two stereoisomeric acids should have been formed (this vol., i, 74), whereas only one, the α-acid, was isolated. In order to obtain the new β-acid, the product of the action of ammonium cyanide on glucosamine hydrochloride was evaporated under reduced pressure, the residue taken up in water, and again evaporated, in which process the cyanohydrin is hydrolysed. The acids are now converted into copper salts, which are separated by water, in which the salt of the α-acid is easily soluble. The copper salt of *β-amino-*d*-glucoheptonic acid*,

$$OH{\cdot}CH_2{\cdot}[CH(OH)]_4{\cdot}CH(NH_2){\cdot}CH(OH){\cdot}CO_2H,$$

crystallises in long, bluish-green prisms, from which the acid can be prepared by treatment with hydrogen sulphide; the acid could not be obtained crystalline, and does not yield any crystalline derivatives except the copper salt; in a five per cent. aqueous solution, $[\alpha]_D = 1°34'$; when warmed with baryta water or with lead oxide, ammonia is evolved. The α-acid, which can be obtained from the soluble copper salt, shows no rotation in a five per cent. aqueous solution; it has a much sweeter taste than the β-acid. K. J. P. O.

Action of Water on the Bromides and Chlorides of Olefines. WILHELM FROEBE and ARMIN HOCHSTETTER (*Monatsh.*, 1902, **23**, 1075—1092).—The following products have been obtained by boiling olefine bromides and chlorides with water.

Methyl *iso*propyl ketone and a glycol or mixture of glycols boiling at 190—200° were obtained from amylene dibromide (which boils at 73° under 17·5 mm. pressure) and from amylene dichloride (which boils at 45—50° under 15 mm. pressure) (compare Niederist, *Annalen*, 1879, **196**, 360).

Methyl *iso*propyl ketone, *iso*amylene $\alpha\beta$-glycol, and, as principal product, γ-methylbutinene are obtained from iso*amylene $\alpha\beta$-dichloride* and *$\alpha\beta$-dibromide.* This bromide, which boils at 68·5—69° under 15 mm. pressure, is formed along with smaller quantities of a *bromoamylene*, boiling at 33—34° under 15 mm. pressure, and higher substitution products by the action of bromine at $-20°$ on γ-methylbutylene (Wischnegradsky, *Annalen*, 1878, **190**, 353).

Methyl *iso*propyl ketone is obtained from β-methylbutylene $\beta\gamma$-dibromide, and dichloride; valeraldehyde could not be detected amongst the products.

Methyl propyl ketone or diethyl ketone and amylene $\beta\gamma$-glycol are obtained from *amylene $\beta\gamma$-dibromide*, which boils at 74° under 17 mm. pressure, and *$\beta\gamma$-dichloride*, which boils at 50—51° under 20 mm. pressure and is obtained by the action of chlorine on the amylene at $-17°$.

γ-Amylene oxide is obtained from amylene-$\alpha\delta$-dibromide and $\alpha\delta$-dichloride.

Amylene $\alpha\delta$-dichloride boils at 58—60° under 15 mm. pressure, and is obtained by heating γ-amylene oxide with concentrated hydrochloric acid at 60°.

δ-Hexylene oxide and δ-hexylene glycol are obtained from δ-hexylene dibromide, which boils at 115—116° under 20 mm. pressure.

The chlorides undergo the reaction with water much more slowly than do the bromides. G. Y.

The Ketonic Nature of Diacetonehydroxylamine and its Oxidation to Nitro*iso*propylacetone. CARL D. HARRIES and UGO FERRARI (*Ber.*, 1903, **36**, 656—659).—Diacetonehydroxylamine (Abstr., 1898, i, 568) reacts with an acetic acid solution of phenylhydrazine yielding a *phenylhydrazone*, $OH\cdot NH\cdot CMe_2\cdot CH_2\cdot CMe{:}N_2HPh$, which crystallises from benzene in colourless plates melting at 120° and practically insoluble in alkalis. When oxidised by Harries and Roeder's method (*Ber.*, 1899, **32**, 3365), the hydroxylamine derivative is converted into ter.-*nitro*iso*propylacetone*, $NO_2\cdot CMe_2\cdot CH_2\cdot COMe$. This is a heavy, pale-yellow oil distilling at 118—119° under 17 mm pressure and having an odour of bitter almonds; it is insoluble in alkalis, but yields a *phenylhydrazone* melting at 97°. When reduced, the nitro-compound is converted into the original hydroxylamino-derivative.

Triacetonedihydroxylamine-phenylhydrazone,

$$N_2HPh{:}C(CH_2\cdot CMe_2\cdot NH\cdot OH)_2,$$

forms a micro-crystalline powder melting at 152°. J. J. S.

Products of Degradation of Starch containing Sugar, formed in the Hydrolysis by means of Oxalic Acid, with Special Reference to Lintner's *iso*Maltose. HEINRICH DIERSSEN (*Zeit. angew. Chem.*, 1903, 16, 122—134).—The products of the hydrolysis of starch by means of oxalic acid have been carefully studied in order to determine accurately the characters of the disaccharide (*iso*maltose) which is always formed. The method of work was in the main identical with that devised by Lintner and Düll (Abstr., 1893, i, 5; 1894, i, 5; and 1895, i, 409, 491); the *iso*maltose was isolated by a long series of crystallisations from definite concentrations of ethyl alcohol instead of the mixture of methyl and ethyl alcohols used by Lintner and Düll. It has been thus ascertained that besides dextrose and a disaccharide, lævulose is formed; the latter has not previously been isolated from the products of the hydrolysis of starch by oxalic acid. Maltose was not found. The disaccharide agrees very closely with Lintner's *iso*maltose; it is a thick syrup having $[\alpha]_D + 140°$ and a reducing power equal to 83 per cent. of that of maltose; in ten per cent. aqueous solution, the sp. gr. is 1·0399, somewhat higher, therefore, than that of maltose, which is 1·0390 under the same conditions. The osazone formed easily soluble, crystalline aggregates melting at 150—153°, and has $[\alpha]_D + 50—55°$; Lintner did not determine the rotation of his *iso*maltose; Fischer's *iso*maltose has $[\alpha]_D - 20°$. The *iso*maltose here described differs from Lintner's in that diastase does not convert it into maltose. The author's experiments demonstrate that dextrose very readily forms compounds with more complex saccharides; thus *iso*maltose separates with the dextrose from solutions of the latter.

The yeast, *Saccharomyces marxianus*, is unable to ferment *iso*maltose. K. J. P. O.

Optically Active Forms of *sec.*-Butylamine. L. G. THOMÉ (*Ber.*, 1903, 36, 582—584).—When the *d*-tartrate, prepared from inactive *sec.*-butylamine, $NH_2·CHMeEt$, is crystallised from water and the first fraction recrystallised, well-formed prisms of the d-*tartrate*, $C_4H_{11}N,C_4H_6O_6,H_2O$, of the *d*-base separate; the pure d-*base* obtained therefrom boils at 63°, has a sp. gr. 0·724 at 20°/4°, and $[\alpha]_D + 7·44$ at 20°. From the mother liquors of the above salt, the corresponding base is liberated and converted into the *l*-tartrate; the pure l-*base* isolated in this way has the same boiling point and sp. gr. as the *d*-form and has $[\alpha]_D - 7·40°$. d-sec.-*Butylamine hydrochloride* crystallises from water or alcohol in long needles and has $[\alpha]_D - 1·13°$; l-sec.-*butylamine hydrochloride* has $[\alpha]_D + 1·12°$.

Gadamer's *d*-butylamine (Abstr., 1901, i, 582), obtained from oil of *Cochlearia*, having $[\alpha]_D + 6·42°$, and giving a hydrochloride with $[\alpha]_D - 2·05°$, was obviously contaminated with a lævorotatory substance.

d-sec.-Butylthiocarbimide, prepared by Hofmann's method, boils at 159°, has a sp. gr. 0·943 at 20°/4°, and $[\alpha]_D + 61·88$ at 20°; l-sec.-*butylthiocarbimide* boils at 159°, has a sp. gr. 0·942 at 20°/4°, and has $[\alpha]_D - 61·80°$. W. A. D.

Oxidation of Aliphatic Amines of the Type $\colon C \cdot NH_2$. EUGEN BAMBERGER and RICHARD SELIGMAN (*Ber.*, 1903, **36**, 685—700).—Like the aromatic amines, the primary aliphatic amines containing tertiary alkyl groups can be oxidised in accordance with the scheme $R \cdot NH_2 \rightarrow R \cdot NH \cdot OH \rightarrow R \cdot NO \rightarrow R \cdot NO_2$.

ter.-Butylamine, $CMe_3 \cdot NH_2$, the simplest primary amine containing a tertiary alkyl group, when oxidised by a cold neutral solution of Caro's persulphuric acid, gave a mixture of the three oxidation products. ter.-*Butylhydroxylamine*, $CMe_3 \cdot NH \cdot OH$, was not isolated, but its presence was proved by the reduction of Fehling's solution, by its oxidation with Caro's solution to blue nitrosobutane, and by the formation, when mixed with benzenediazonium chloride, of a yellow, crystalline precipitate of the azohydroxyamide, $CMe_3 \cdot N(OH) \cdot N_2Ph$, which gave a permanent, deep indigo-blue colour with dilute ferric chloride. ter.-*Nitrosobutane*, $CMe_3 \cdot NO$, prepared by oxidising during six minutes only single grams of the amine and at once separating and drying the blue ethereal solution, is so exceedingly volatile that it distils completely with the ether, leaving behind a residue which consists mainly of nitrobutane; the yield of the nitroso-compound is very small and the greater part of the amine can be recovered unchanged. Although its ethereal solution is deep blue in colour, the nitroso-compound is left behind in white, silky needles when the ether is removed by a current of air, the complete evaporation of the solvent being indicated by the abrupt disappearance of the blue colour from the residue. Freshly prepared solutions in benzene of the nitrosobutane are colourless and have a molecular weight (by the cryoscopic method) very little below that required for a double molecule (after 1 minute, obs., 166·3; calc., 174), but as the blue colour develops the molecular weight falls, becoming steady after about four hours, when the colour has fully developed, at a value but little above that required for a single molecule (after 226 minutes, obs., 95·2; calc., 87); a complete curve is given showing the change of mol. wt. with time. The depolymerisation is brought about immediately if the solution is warmed, but is very much retarded by exposing the solution to sunlight. In a sealed tube, the nitroso-compound melts at 76—76·5°, and at 80—82° distils to the upper part of the tube to blue drops, which quickly solidify to colourless, glistening prisms; in an open tube, it sublimes without melting at 76°; this behaviour is similar to that of nitrosobenzene, which sublimes without melting when heated under 10 mm. pressure. Nitrosobutane has no pungent smell, but a pleasant, camphor-like odour. It is soon decomposed, especially when in the blue monomolecular form. Tertiary nitrobutane was obtained as a yellow oil, volatile with steam and with a somewhat pungent odour; it was identified by reduction to butylamine and butylhydroxylamine.

ter.-Amylamine is oxidised in a similar manner, ter.-*amylhydroxylamine*, $CMe_2Et \cdot NH \cdot OH$, and nitropentane, $CMe_2Et \cdot NO_2$, being identified by qualitative tests. ter.-*Nitrosopentane*, $CMe_2Et \cdot NO$, was prepared by oxidising the amine with Caro's solution for six minutes; most of the ether was distilled off through a fractionating column and the rest was removed by a current of air. The nitrosopentane separates in glistening, colourless tablets, melts at 50—50·5° in an

open tube, and at 70° distils in the form of blue drops which solidify to colourless crystals; the change of molecular weight in freezing benzene solution as the colour develops is even more striking than in the previous case, the initial value at 45 seconds being 201·2 (calc., 202) and the constant value 98·3 (calc., 101).

Unlike the preceding amines, diacetonamine, $NH_2 \cdot CMe_2 \cdot CH_2Ac$, can be made to give a sixty per cent. yield of the corresponding nitroso-compound; in this case, it is possible to add alkali during the oxidation in order to neutralise the sulphuric acid produced by reduction of persulphuric acid and so to liberate the base, and, moreover, the nitroso-compound is much less volatile and is readily separated from the solvent ether. It crystallises from light petroleum in clear, colourless, glassy, triclinic tablets, the angle of which is $91\frac{1}{2}°$, the optical properties of the crystals being also described; it melts at 75·5°, as described by Harris and Jablonski (Abstr., 1898, i, 400), to a blue liquid. The solutions are at first colourless and bimolecular, the initial molecular weight after 30 seconds in benzene solution being 257 (calc., 258) and the final value 133 (calc., 129). It is remarkable, however, that the depolymerisation takes place more rapidly in benzene than in methyl alcohol or acetic acid, more rapidly in chloroform or acetone than in acetic acid or ethyl acetate, and more rapidly in anhydrous acetic or formic acid than in the moist solvents; the aqueous solution may remain almost colourless for a month and becomes coloured only after 15—20 seconds when heated. The colourless solutions are odourless, whilst the coloured solutions have a pungent odour. The unimolecular solid, prepared by chilling the blue fused mass, is much more soluble in light petroleum than the colourless, bimolecular crystals, and its solution gradually deposits (at constant temperature and with no evaporation of the solvent) colourless prisms. The colourless compound is much more stable in sunlight than the coloured compound and is far less volatile, so that it can be kept in a vacuum desiccator for 48 hours without loss, whilst the coloured compound is exceedingly volatile and is carried over in small quantities with ether vapour. A further point of difference is in the decomposition which occurs in a formic acid solution whenever the blue compound is present, carbon dioxide and nitrogen being liberated; this decomposition takes place spontaneously in the anhydrous acid, far more slowly in cold 90 per cent. acid (in which the blue colour is but slowly developed), explosively on warming the colourless solution, and also on adding the blue solid to the acid.

Triphenylmethylamine, $CPh_3 \cdot NH_2$, could not be oxidised in this way. T. M. L.

Oxidation of Aliphatic Amines of the Type $\colon CH \cdot NH_2$. EUGEN BAMBERGER and RICHARD SELIGMAN (*Ber.*, 1903, **36**, 701—710). —*iso*Propylamine, $CHMe_2 \cdot NH_2$, is oxidised by a neutral solution of Caro's persulphuric acid to acetoxime; *sec.*-nitropropane was not formed, but small quantities of propyl-ψ-nitrole (needles melting at 76° to a blue oil) were isolated. γ-Aminopentane, $CHEt_2 \cdot NH_2$, was oxidised to diethylketoxime, $CEt_2 \colon N \cdot OH$, and in hot solution to the ψ-nitrole, $NO \cdot CEt_2 \cdot NO_2$. Benzhydrylamine, $CHPh_2 \cdot NH_2$, was oxidised to

benzophenoneoxime. α-Phenylethylamine, $CHPhMe\cdot NH_2$, was oxidised to acetophenoneoxime, with its decomposition products (phenol, acetic acid, carbon dioxide, formic acid, and benzoic acid) and α-nitro-α-phenylethane.

α-Nitro-α-phenylethane, $CH_3\cdot CHPh\cdot NO_2$, boils at 115—115·5° (corr.) under 11 mm. pressure; the *sodium* salt of the ψ-nitro-compound forms white crystals; the *ψ-nitro*-compound itself, $CMePh\colon NO_2H$, is precipitated by hydrochloric acid from a solution of the sodium salt in snow-white, glistening needles, and softens at 45° with development of a sky-blue colour; the *ψ-nitrole*, $NO\cdot CMePh\cdot NO_2$, was obtained as a semi-solid, greenish-blue mass, which rapidly decomposed with formation of acetophenone and nitric oxide.

p-*Nitrobenzeneazo-α-nitro-α-phenylethane*, $NO_2\cdot CMePh\cdot N_2\cdot C_6H_4\cdot NO_2$, crystallises from chloroform on adding light petroleum in orange-yellow rosettes, or from chloroform alone in well-formed, transparent prisms with a greenish shimmer; it melts at 118·5—119°.

ac-Tetrahydro-β-naphthylamine, $C_6H_4<\begin{matrix}CH_2\cdot CH\cdot NH_2\\ |\\ CH_2\cdot CH_2\end{matrix}$, was oxidised by a neutral solution of Caro's persulphuric acid to the corresponding oxime, $C_{10}H_{10}\colon NOH$, which was identified by hydrolysis to hydroxylamine and the ketone, $C_{10}H_{10}O$. T. M. L.

Determination of the Structure of Amines by means of Caro's Persulphuric Acid. EUGEN BAMBERGER (*Ber.*, 1903, 36, 710—714).—The oxidation of amines of the type $R\cdot CH_2\cdot NH_2$ to hydroxamic acids by means of Caro's persulphuric acid can be used as a qualitative test for this class of amines. A few amines of the type $\colon CH\cdot NH_2$ give the same result, but probably because the intermediate oxime undergoes an isomeric change of the Beckmann type, for instance, camphoroxime, $C_8H_{14}<\begin{matrix}CH_2\\ |\\ C\colon NOH\end{matrix}$, yields the amine,

$$C_8H_{14}<\begin{matrix}CO_2H\\ CH_2\cdot NH_2\end{matrix}.$$

The conclusion is drawn that if an amine does not give this reaction it probably does not contain the group $\cdot CH_2\cdot NH_2$, but that the occurrence of the action does not prove the presence of the group. The test is applicable to amino-acids.

A few imines give the hydroxamic acid reaction when oxidised, but this is probably due to elimination of a methyl group by oxidation to formaldehyde. T. M. L.

Nitrogentricarboxylic Esters and Syntheses by means of Ethyl Sodiocarbamate. OTTO DIELS (*Ber.*, 1903, 36, 736—747).—*Ethyl nitrogentricarboxylate*, $N(CO_2Et)_3$, prepared by the addition of ethyl chlorocarbonate (2 mols.) to an ethereal solution of ethyl carbamate (1 mol.) in which sodium (2 atoms) has been dissolved, boils at 146—147° under 12 mm. pressure, and has a sp. gr. 1·1432 at 21° and n_D 1·42955. When 1 mol. of ethyl carbamate interacts with 1 atom of sodium and 1 mol. of ethyl chlorocarbonate, instead of obtaining pure ethyl iminodicarboxylate, $NH(CO_2Et)_2$

(compare Kraft, Abstr., 1891, 42), a mixture of this substance with unchanged ethyl carbamate and a larger proportion of ethyl nitrogentricarboxylate is produced; that the production of the latter is due to the chlorocarbonate acting on sodium ethyl iminodicarboxylate, formed thus, $NHNa{\cdot}CO_2Et + NH(CO_2Et)_2 = NNa(CO_2Et)_2 + NH_2{\cdot}CO_2Et$, and not to the interaction of the chlorocarbonate with a disodium derivative of ethyl carbamate initially produced, is shown by the quantity of unchanged ethyl carbamate remaining after the action, taken together with the fact that one atom of sodium fully saturates 1 mol. of the carbamate. Moreover, purified ethyl iminodicarboxylate is converted by potassium and ethyl chlorocarbonate in xylene solution into ethyl nitrogentricarboxylate, and ethyl potassiocarbamate by ethyl iminodicarboxylate into ethyl carbamate and potassium ethyl iminodicarboxylate. When 2 mols. of ethyl sodiocarbamate, and 1 mol. of ethyl chlorocarbonate interact in ethereal solution, ethyl iminodicarboxylate and ethyl carbamate are the sole products.

Nitrogentricarboxylic acid cannot be obtained by hydrolysing its ester with aqueous potassium hydroxide at 0° and acidifying with dilute sulphuric acid; under these conditions, it is decomposed, giving alcohol, carbon dioxide, and ethyl iminodicarboxylate. With aqueous ammonia, ethyl nitrogentricarboxylate gives, not the corresponding amide, but ethyl carbamate and ethyl allophanate, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO_2Et$; by 50 per cent. aqueous hydrazine hydrate, it is converted similarly into *ethyl hydrazinecarboxylate*, $NH_2{\cdot}NH{\cdot}CO_2Et$, and the *dihydrazide*, $NH(CO{\cdot}NH{\cdot}NH_2)_2$, of iminodicarboxylic acid. The former of these is an oil which boils at 92° under 13 mm. pressure, and the latter crystallises from water on adding alcohol in white prisms, and melts and decomposes at 199—200° (corr.); on the addition of acid to its aqueous solution, it is converted, by the loss of 1 mol. of hydrazine, into urazole.

Ethyl sodiocarbamate and ethyl chloroacetate in absolute ether give, not ethyl urethanodiacetate, $CO_2Et{\cdot}N(CH_2{\cdot}CO_2Et)_2$, but ethyl chloroacetylcarbamate, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CO_2Et$. Similarly, ethyl sodiocarbamate with ethyl oxalate gives ethyl oxalyldiaminoformate, $C_2O_2(NH{\cdot}CO_2Et)_2$ (Hantzsch, Abstr., 1894, i, 363), and, with ethyl phenylacetate, *phenacetyl urethane*, $CH_2Ph{\cdot}CO{\cdot}NH{\cdot}CO_2Et$; this crystallises from water in thin, lustrous prisms, melts at 113° (corr.), and when heated for 6 hours at 180° gives phenylacetimide,

$$NH(CO{\cdot}CH_2Ph)_2$$

(Colby and Dodge, Abstr., 1891, 409), and ethyl iminodicarboxylate. At 230°, the latter substance is resolved into cyanuric acid (compare Kraft, *loc. cit.*), which is then the principal product. W. A. D.

Thiocarbamide Derivatives of Univalent Metallic Salts. Arthur Rosenheim and Willy Loewenstamm (*Zeit. anorg. Chem.*, 1903, **34**, 62—81).—When a suspension of cuprous chloride is boiled with thiocarbamide, white, prismatic crystals of *cuprotrithiocarbamide chloride*, $[Cu(CSN_2H_4)_3]Cl$, are obtained. The same substance is produced by adding cupric chloride to a solution of thiocarbamide. The salt is easily soluble in water, and the addition of a highly dissociated

chloride very readily causes its precipitation, indicating that in the aqueous solution it is very little dissociated. When thiocarbamide is added to a solution of cupric chloride, or when thiocarbamide is treated with excess of cuprous chloride, insoluble needles of *cupromonothiocarbamide chloride*, $[Cu(CSN_2H_4)]Cl,\frac{1}{2}H_2O$, are formed. This is soluble in a solution of the trithiocarbamide chloride, and from the solution prismatic needles of *cuprodithiocarbamide chloride*,

$$[Cu(CSN_2H_4)_2]Cl,$$

separate. *Cuprotrithiocarbamide bromide*, $[Cu(CSN_2H_4)_3]Br$, separates in white, hexagonal crystals from a solution obtained by shaking cuprous bromide with saturated thiocarbamide solution. It is soluble in water, and when the solution is treated with hydrobromic acid slender needles of *cupromonothiocarbamide bromide*,

$$[Cu(CSN_2H_4)]Br,4H_2O,$$

are deposited. If a saturated solution of thiocarbamide is boiled with cuprous iodide, a yellow oil deposits on cooling, which, after remaining for some days over sulphuric acid, changes into transparent, hexagonal crystals of *cuprotrithiocarbamide iodide*, $[Cu(CSN_2H_4)_3]I$. From cuprous cyanide, *cuprodithiocarbamide cyanide*, $[Cu(CSN_2H_4)_2]CN,H_2O$, and from cupric nitrate, a *pentathiocarbamide* derivative,

$$[Cu_2(CSN_2H_4)_5](NO_3)_2,2H_2O,$$

have been isolated. *Cuprothiocarbamide sulphate*,

$$[Cu_2(CSN_2H_4)_5]SO_4,2H_2O,$$

has been obtained from (*a*) a solution of thiocarbamide and cupric sulphate, (*b*) a solution of cuprotrithiocarbamide chloride and sulphuric acid, and (*c*) a concentrated solution of cuprothiocarbamide hydroxide and sulphuric acid; it is a white salt which decomposes readily with formation of cuprous sulphide. The *oxalate*, $[Cu(CSN_2H_4)_3]_2C_2O_4$, the *hydrogen phosphate*, $[Cu(CSN_2H_4)_3]_2HPO_4$, and the *hydrogen arsenate*, $[Cu(CSN_2H_4)_3]_2HAsO_4$, have also been prepared.

By similar processes, the following silver and thallous compounds have been obtained: $[Ag(CSN_2H_4)]CN$; $[Ag_2(CSN_2H_4)_5]SO_4,2H_2O$; $[Ag(CSN_2H_4)_3]_2HPO_4$; $[Tl(CSN_2H_4)_4]Cl$; $[Tl(CSN_2H_4)_4]Br$; $[Tl_2(CSN_2H_4)_7]SO_4,2H_2O$; $[Tl(CSN_2H_4)_4]NO_3$; and $[Tl(CSN_2H_4)_4]_2CO_3$.

Reynolds (Trans., 1891, **59**, 384) has described a series of ammonium derivatives of the type $NH_4(CSN_2H_4)_4R$, and the authors have investigated the ammonium compounds and the compounds of the alkali metals to find if only salts of this type can be obtained. When ammonium nitrate and excess of thiocarbamide are boiled in alcoholic solution, *ammoniumtetrathiocarbamide nitrate*, $[NH_4(CSN_2H_4)_4]NO_3$, is produced. It forms needle-shaped crystals which are soluble in water, but it is easily decomposed into its components. No other ammonium salt has been isolated in a pure state. The corresponding potassium salt is produced in a similar manner. With cæsium chloride, a *hexathiocarbamide* derivative, $[Cs(CSN_2H_4)_6]Cl$, is formed.

The compounds described are undoubtedly to be regarded as salts of a complex cathion, and the authors regard the alkali metallic derivatives as the first examples of complex cathions of the strongly electropositive alkali metals.

Hantzsch's results (Abstr., 1901, ii, 54) on the diminution of the conductivity of electrolytic solutions by the addition of thiocarbamide

are discussed, and it has been found that the conductivity of solutions of potassium chloride, potassium bromide, ammonium chloride, bromide, nitrate, and sulphate is diminished by the addition of thiocarbamide, thus indicating the formation of complex cathions of the alkali metals. J. McC.

Preparation, Properties, and Desulphuration of Ethylenethiocarbamide. H. KLUT (*Arch. Pharm.*, 1902 **240**, 675—678).—Ethylenethiocarbamide, $CS{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C_2H_4$, can be prepared from commercial 10 per cent. aqueous ethylenediamine solution by preparing the hydrochloride from this, recrystallising it from water, dissolving it in a little water, adding the equivalent amount of sodium hydroxide and plenty of alcohol, leaving it overnight, filtering from the precipitated sodium chloride, and treating the filtrate as directed by Hofmann (this Journal, 1872, 501).

The thiocarbamide is very stable towards chemical reagents, and when treated with mercuric oxide, freshly precipitated but still containing a little alkali, it is decomposed almost quantitatively into carbon dioxide, hydrogen sulphide, and ethylenediamine.

It is possible to replace the sulphur by oxygen by digesting the thiocarbamide with water and freshly precipitated mercuric oxide on the water-bath. The filtered solution is made slightly acid with hydrochloric acid and precipitated with sodium picrate in the cold. The smaller portion of the precipitate dissolves in boiling water; after recrystallisation, this is found to melt and decompose at 207—209° and to have the composition of *ethylenecarbamide picrate*, $C_3H_6ON_2,C_6H_3O_7N_3$. The yield is small. C. F. B.

Acid Function of Hydroxyloxamide. HUGO SCHIFF (*Annalen*, 1903, **326**, 259).—It has been stated that hydroxyloxamide (aminoximoxalic acid) only behaves as a monobasic acid after the addition of formaldehyde (Abstr., 1902, i, 429), whilst it has been shown by Pickard, Allen, Bowdler, and Carter (Trans., 1902, **81**, 1566) that the substance has the same property in the absence of the aldehyde. The discrepancy was due to the fact that the material originally used was an old preparation which had absorbed ammonia. With a pure specimen, the results obtained were in accord with those of the English chemists. K. J. P. O.

A New Electrochemical Synthesis of Hydrogen Cyanide. J. GRUSZKIEWICZ (*Zeit. Elektrochem.*, 1903, **9**, 83—85).—Sparks from an induction coil are passed between platinum wires, which are so close to each other that a small arc is formed, in a mixture of hydrogen, carbon monoxide, and nitrogen. Hydrogen cyanide is formed, the velocity of formation increasing with the quantity of carbon monoxide present. A mixture containing about 50 per cent. of carbon monoxide and 25 per cent. of nitrogen gives the best result. T. E.

Preparation of Alkali Cyanides from Metallic Cyanogen Compounds. BRITISH CYANIDES CO. (D.R.-P. 132294).—Cyanides of the heavy metals, thiocyanates, or ferrocyanides are heated in a current of hydrogen or water-gas, at first gently to expel moisture, then more strongly, finishing at 500—600°. In the case of thiocyanates, sufficient copper is mixed with the mass to fix all the sulphur as cuprous sulphide. Hydrogen cyanide distils off and is absorbed in a solution of an alkali hydroxide. The thiocyanates, zinc cyanide, and Prussian blue are especially suitable for this process. Metallic ferrocyanides yield only a portion of their cyanogen. C. H. D.

[Action of Iron in the Formation of Cyanides.] ERNST TÄUBER (*Chem. Centr.*, 1903, i, 434; from *Chem. Ind.*, **26**, 26—27. Compare Abstr., 1901, ii, 107, and Remsen, *Amer. Chem. J.*, 1881, **3**, 134).—Experiments on the formation of cyanide were made by passing nitrogen through a heated tube containing various mixtures of (*a*) lamp-black, coal, coke or charcoal prepared from sugar or wood shavings, (*b*) calcined sodium or potassium carbonate, hydroxides of the alkali or alkaline earth metals, and (*c*) powdered iron. The tube was kept at a dark to moderate red heat, and in some cases hydrogen was first passed through it in order to reduce any oxide of iron to the metallic state. The best yield was obtained with a mixture of wood charcoal and sodium carbonate prepared by moistening 3 parts of wood shavings with a solution of one part of calcined sodium carbonate and carbonising. After heating for $1\frac{1}{4}$ hours, about 10 per cent. of the carbonate was converted into cyanide. Very variable results were obtained when coke was used, and coal appeared even less suitable. A mixture of ordinary commercial powdered iron with three parts of sodium carbonate was employed; a lower proportion of iron was found to give less cyanide and a higher did not increase the yield. Nitrogen prepared from ammonium nitrite gave the best result, probably owing to admixture with small quantities of oxides of nitrogen; after purification, it behaved precisely like nitrogen obtained from the atmosphere. E. W. W.

Two Acids containing Phosphorus derived from Methyl Ethyl Ketone. CHARLES MARIE (*Compt. rend.*, 1903, **136**, 234—235).—Methyl ethyl ketone condenses with hypophosphorous acid in the same manner as does acetone, but only forms a monoketonic acid corresponding with hydroxy*iso*propylhypophosphorous acid, and yields no diketonic acid. Hypophosphorous acid (1 mol.) is heated with an excess of methyl ethyl ketone (4 mols.) until a boiling point of 86° is attained; after removing the excess of the ketone and the oily ethereal products of the reaction, the aqueous solution of the residue is neutralised with lead carbonate and yields both a soluble and an insoluble lead salt. On decomposing the solution of the former with hydrogen sulphide, the acid, $COMeEt,H_3PO_2$, is obtained as a colourless, hygroscopic syrup, not solidifying at $-20°$; its salts resemble those of hydroxy*iso*propylhypophosphorous acid (Abstr., 1901, i, 635; 1902, i, 71, 255). When heated with benzaldehyde at 100°, the acid, $CHOPh,COMeEt,H_3PO_2$,

is produced. The insoluble lead salt, which is only formed in small amount, is the *derivative* of the hydroxyphosphinic acid, $COMeEt,H_3PO_3$; it is more readily prepared by oxidising the hydroxyhypophosphorous acid by bromine water; it crystallises in leaflets melting at 158—159° and yields a silver salt, $COMeEt,AgH_2PO_3$, as an insoluble, crystalline precipitate. When treated with benzoyl chloride in the presence of pyridine, an oily *benzoyl* derivative is formed. K. J. P. O.

Compounds of Methylarsinic Acid with Ferric Hydroxide. M. Leprince (*J. Pharm. Chim.*, 1903, [vii], 17, 22—26).—By the addition of ferric hydroxide to warm solutions of methylarsinic acid, insoluble, colourless acid, and soluble, brownish-red basic, salts appear to be formed, but from the gradual change in properties on successive addition of hydroxide and the behaviour on dialysis, it is concluded that these salts are not definite. G. D. L.

Action of Sulphur on Toluene and Xylene. Louis Aronstein and A. S. van Nierop (*Rec. trav. chim.*, 1902, 21, 448—459).—The anomalous results of the determination of the molecular weight of sulphur by Aronstein and Meihuizen (Abstr., 1900, ii, 341) in toluene and xylene solutions are due to the chemical action of the sulphur on those hydrocarbons, hydrogen sulphide being disengaged on prolonged boiling of the solutions, less readily, however, with *m*-xylene than with toluene or *p*-xylene. Under these conditions, stilbene is formed from the toluene, whilst after 12 days' heating at 250—300° stilbene and tetraphenylthiophen are produced. On prolonged heating with sulphur at 200—210°, *p*- and *m*-xylenes both yield the corresponding dimethylstilbenes and dimethyldibenzyls. *m*-Dimethylstilbene melts at 55—56° and gives a dibromide melting at 167—168°. *p*-Dimethylstilbene displays dimorphism, crystallising either in large crystals or in very small leaflets of silky lustre with a violet fluorescence. *p*-Dimethylstilbene is reduced by hydrogen sulphide at 200° to *p*-dimethyldibenzyl, and the latter hydrocarbon is converted into *p*-dimethylstilbene on similar treatment with sulphur.

The authors regard the formation of stilbenes and hydrogen sulphide as the primary change in the action of sulphur on toluene and the xylenes. G. D. L.

***n*-Propylbenzene.** August Klages (*Ber.*, 1903, 36, 621—622).—It was previously stated (Abstr., 1902, i, 666) that propenylbenzene (α-allylbenzene) is reduced by sodium and alcohol to cumene (*iso*propylbenzene), whereas normal propylbenzene is formed. Propenylbenzene (α-allylbenzene) was prepared from phenyl ethyl carbinol, which was obtained by Grignard's method from benzaldehyde and ethyl iodide, and boils at 108—110° under 15 mm. pressure; the carbinol was converted into the chloride, CHPhEtCl, which is then heated with pyridine (2 mols.) under pressure at 125°; by this treatment, the first formed additive product of pyridine and the chloride is completely decomposed. Propenylbenzene boils at 72—74° under 15 mm. pressure and has a sp. gr. 0·9338 at 14°/4° and n_D 1·5482 at 14°. According to

Perkin (Trans., 1891, 59, 1010), propenylbenzene boils at 174—175° at the ordinary pressure, whereas the pure product begins to distil at 166° and gives a turbid distillate; polymerisation has probably taken place, and the product is not readily reduced to *n*-propylbenzene. The propylbenzene prepared by reducing propenylbenzene by sodium and boiling absolute alcohol boils at 67—68° under 15 mm. and at 157·5° under 765 mm. pressure, and has a sp. gr. 0·8680 at 13°/4° and n_D 1·4984 at 13°. K. J. P. O.

Ring-system of Benzene. IV. Hugo Kaufmann and Alfred Beisswenger (*Ber.*, 1903, **36**, 561—570).—Benzenoid mononitro-compounds, especially those of phenol and phenol ethers, have their colour increased by dissolution in concentrated sulphuric acid; the increase of colour occurs simultaneously with an increase in luminescence towards the Tesla-rays (Abstr., 1902, ii, 191). When the number of nitro-groups is increased or a halogen substituted in a mononitro-compound, there is a diminution in both these respects. A carbonyl group in the nucleus increases the coloration with sulphuric acid much more than a nitro-group.

Hydrocarbons and phenols of the benzene series as a rule dissolve without coloration, but the ethers of quinol and resorcinol give yellow solutions; α- and β-naphthol, their ethers, and the ethers of dihydroxy-naphthalenes give yellow to orange tones. The anilines, aminophenols, anisidine, and phenetidine give colourless solutions. In the case of compounds containing oxygen and nitrogen there is parallelism between increase of colour and luminescence to the Tesla-rays.

In the case where salts are formed of coloured amines without an alteration in the chromophorous group, the base is more highly coloured than the salt; this is verified by the author with bases containing the chromophores NO_2, CO, CO_2H, SO_2. With phenols under the same restriction, salt formation is accompanied by an increase in colour. If the substance forming the salt possesses both acid and basic properties, there is an increase of colour on the addition of bases and a decrease on the addition of acids.

1 : 5-*Dimethoxynaphthalene*, obtained by methylating the corresponding dihydroxy-compound, forms long, colourless needles, melts at 174—175°, and can be purified by sublimation; 2 : 3-*dimethoxynaphthalene* crystallises from light petroleum in aggregates of needles melting at 116·5°, and 2 : 6-*dimethoxynaphthalene* from methyl alcohol in nacreous plates melting at 149·5°. W. A. D.

Chlorination of Substituted Aromatic Hydrocarbons by means of Ammoniacal Lead Tetrachloride. Alphonse Seyewetz and P. Trawitz (*Compt. rend.*, 1903, **136**, 240—243. Compare Seyewetz and Biot, this vol., i, 157).—The use of plumbic ammonium chloride, $PbCl_4,2NH_4Cl$, as a chlorinating agent has been extended to aromatic compounds which already contain either chlorine, bromine, and iodine radicles, or the nitro-group. Benzyl chloride is converted into benzylidene chloride and a small quantity of benzotrichloride; benzotrichloride only yields traces of *p*-chlorobenzotrichloride, which was recognised by converting into *p*-chlorobenzoic acid. *o*- and *p*-Chloro-

toluenes are readily attacked at the boiling points, giving *o*- and *p*-chlorobenzyl chlorides; these substances being respectively oxidised to *o*- and *p* chlorobenzoic acids. Chlorobenzene is very slowly acted on at its boiling point by the tetrachloride; heating under pressure only led to the formation of a very small amount of *p*-dichlorobenzene (m. p. 53°). In the case of bromobenzene, bromine was eliminated, a mixture of chlorobenzene and tribromochlorobenzene being produced. At its boiling point (190°), iodobenzene yields chlorobenzene and iodine, but at 100° iodobenzene dichloride, $IPhCl_2$, is formed. When heated under pressure at 210°, neither nitrobenzene nor *o*-nitrotoluene reacts with the tetrachloride. K. J. P. O.

Preparation of *o*-Chlorotoluene. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 133000).—*p*-Toluenesulphonic chloride is readily chlorinated in the *o*-position by the action of dry chlorine in the presence of antimony or ferric chloride or iodine. o-*Chlorotoluene*-p-*sulphonic chloride* melts at 38° (compare Limpricht and Paysan, Abstr., 1884, 72). On warming with alkaline solutions, or, better still, by boiling with 80 per cent. sulphuric acid, it yields *o*-chlorotoluene. C. H. D.

[Constitution of Primary Dinitrohydrocarbons.] ROLAND SCHOLL (*J. pr. Chem.*, 1903, [ii], 67, 200).—Polemical. A reply to Ponzio (this vol., i, 161). G. Y.

Allylbenzene and Allyl-*p*-xylene. FRANZ KUNCKELL and WILHELM DETTMAR (*Ber.*, 1903, 36, 771—773. Compare Tiemann, *Ber.*, 1878, 11, 672; Perkin, Trans., 1891, 59, 1010; Klages, this vol., i, 329).—*a Chloro-β-bromoallylbenzene*, CPhCl:CBrMe, is obtained when bromopropiophenone is heated with phosphorus pentachloride at 110°, the product extracted with ether, and slowly distilled under reduced pressure. It is a pale yellow oil, which distils at 135—140° under 11 mm. pressure, and when its ethereal solution is mixed with sodium wire, gives a good yield of allylbenzene. This distils at 167—170° and has a sp. gr. 0·908 at 15°. In order to obtain a good yield of the hydrocarbon, it is necessary that the ether shall contain 1—2 per cent. of alcohol. *a-Chloro-β-bromoallyl*-p-*xylene*, $C_6H_3Me_2$·CCl:CBrMe, distils at 137—143° under 18 mm. pressure and at 258—261° under atmospheric pressure, and has a sp. gr. 1·199 at 20°. On treatment with ether and sodium wire, it yields *allyl*-p-*xylene*, which distils at 84—88° under 8 mm. pressure and at 219—223° under atmospheric pressure, and has a sp. gr. 0·9259 at 22°. Its *dibromide* is a thick, yellow oil distilling at 163—166° under 17 mm. pressure and having a sp. gr. 1·457 at 16°. J. J. S.

1^1-Butenylbenzene[-α-phenyl-Δ^a-butylene]. FRANZ KUNCKELL and KARL SIECKE (*Ber.*, 1903, 36, 774—775. Compare Perkin, this Journal, 1877, 32, 667).—*a-Chloro-β-bromobutenylbenzene*, CPhCl:CBrEt, obtained by the action of phosphorus pentachloride on α-bromobutyrophenone at 120°, is a pale yellow liquid distilling at 140—145° under 8 mm. pressure. On treatment with sodium wire and ether, it yields

butenylbenzene, CHPh:CHEt. This distils at 70—71° under 8 mm or at 188—190° under atmospheric pressure, and has a sp. gr. 0·9065 at 13°. Its *dibromide* melts at 70—71°.

When α-chloro-β-bromobutenylbenzene is boiled with concentrated alcoholic potash, an oil distilling at 102—105° under 8 mm. or at 232—234° under atmospheric pressure, and having a sp. gr. 1·1434 at 14° is obtained. It is probably phenylchloromethylallene,

CPhCl:C:CHMe.

J. J. S.

Impurities of Technical Indene and a New Synthesis of Truxene. MAX WEGER and A. BILLMANN (*Ber.*, 1903, 36, 640—645).—By the aid of the hydroxybenzylbenzylidene derivative, Thiele (Abstr., 1901, i, 76) has shown that technical indene contains 65 per cent. of pure indene, and not 90 per cent. as previously supposed. It has, however, been found that the amount of indene in the technical product depends on the age of the specimen, and, when the indene has been freshly prepared from coal tar, amounts to 80 per cent. In order to obtain a quantitative yield of hydroxybenzylbenzylideneindene and therefore to isolate the whole of the indene present in the technical material, the indene and the benzaldehyde should be diluted with a little alcohol and shaken with potassium hydroxide, and the impurities then removed by distilling with steam. This distillate contains coumarone (10—17 per cent.) and hydrindene (5 per cent.); this leaves about 5 per cent. of the original technical indene unaccounted for. On keeping, indene rapidly absorbs oxygen, acquires an acid reaction, and reduces silver; treated with alcohol, the partially oxidised indene gives an insoluble portion, whilst pure indene is completely soluble; according to its age, technical indene contains from about 1 per cent. to 4 per cent. of oxygen; when freely exposed to the air or when air is passed through indene, the percentage of oxygen may rise to 16—17. These oxidised products do not distil with steam, and consequently are left with the hydroxybenzylbenzylidene derivative.

Both on heating and on keeping, indene suffers polymerisation, giving substances which are insoluble in alcohol. Coumarone undergoes no such change.

From the residue of the distillation of indene, truxene, $C_{18}H_{12}$, has been isolated; it is probably formed together with hydrindene as follows: $4C_9H_8 = C_{18}H_{12} + 2C_9H_{10}$. K. J. P. O.

Decomposition of Polymeric Compounds: Truxene from Coumarone-tar. GUSTAV KRAEMER (*Ber.*, 1903, 36, 645—648. Compare preceding abstract).—The opinion is expressed that the conversion of indene into truxene and hydrindene (*loc. cit.*) is an example of a process which plays an important part in the formation of the heavy oils and greases, both in natural oils and in the products of distillation of coal. Thus "bakunin," $C_{20}H_{36}$, which has been recently described by Kraemer and Spilker (Abstr., 1900, i, 617) as a constituent of Russian petroleum, is probably identical with the condensation product formed from decylene. K. J. P. O.

Action of Zinc on Triphenylchloromethane. JAMES F. NORRIS and LLORA R. CULVER (*Amer. Chem. J.*, 1903, 29, 129—140. Compare Abstr., 1901, i, 198).—A quantitative study of the reaction between zinc and triphenylchloromethane has shown that the reaction is very complicated and that slight variations in the conditions have a marked influence on the result. It was found that a larger quantity of zinc is used than that demanded by Gomberg's equation, $2C(C_6H_5)_3Cl + Zn = 2C(C_6H_5)_3- + ZnCl_2$, that more oxygen is absorbed than is contained in the peroxide, and that the percentage of peroxide produced is less than that found by Gomberg.

In order, if possible, to remove the elements of hydrogen chloride from triphenylchloromethane without the application of heat, a mixture of triphenylchloromethane and pyridine was dissolved in ethyl acetate and the solution left for a few days; the *compound*, $C(C_6H_5)_3Cl,C_5H_5N$, which separated in large, pink crystals, melts at 167—167·5°, and is decomposed by water with formation of triphenylcarbinol and pyridine.

E. G.

Bromination and Nitration of Certain Derivatives of Methylaniline and Ethylaniline. JAN J. BLANKSMA (*Rec. trav. chim.*, 1902, 21, 413—418. Compare Abstr., 1902, i, 600).—When heated with alcoholic ammonia on the water-bath, 1-bromo-3 : 4-dinitrobenzene gives Körner's 3-bromo-6-nitroaniline (*Jahrb.*, 1875, 333), which, on bromination in acetic acid solution, gives Schiff's 3 : 4-dibromo-6-nitroaniline (Abstr., 1891, 45) and 2 : 3 : 4-tribromo-6-nitroaniline, the latter melting at 166° and not at 161° as stated by Körner.

When treated with methylamine, 1-bromo-3 : 4-dinitrobenzene gives 3-bromo-6-nitromethylaniline melting at 115°, and this on bromination, yields successively 3 : 4-*dibromo*-6-*nitromethylaniline*, which forms orange-red crystals melting at 165°, and 2 : 3 : 4-*tribromo*-6-*nitromethylaniline*, melting at 128°. The corresponding derivatives of ethylaniline, prepared in a similar manner, melt at 90°, 128°, and 130° respectively.

3 : 4-*Dibromo*-2 : 6-*dinitrophenylmethylnitroamine*, obtained by the action of fuming nitric acid on 3 : 4-dibromo-6-nitromethylaniline, forms colourless crystals melting at 140°; on treatment with methylamine, this is converted into 4-*bromo*-2 : 6-*dinitro*-3-*methylaminophenylmethylnitroamine*, which forms yellow crystals melting at 179°, and when treated with fuming nitric acid yields 4-*bromo*-2 : 6-*dinitro*-m-*phenylenedimethyldinitroamine*, forming colourless crystals melting and decomposing at 173°.

p-*Nitrobenzomethylamide*, prepared by the action of *p*-nitrobenzoy chloride on methylamine, forms colourless crystals melting at 218°; the corresponding *m*-nitrobenzmethylamide melts at 174° and is identical with the compound previously obtained by Romburgh (Abstr., 1886, 546) by nitrating benzomethylamide. G. D. L.

1 : 2-Dichloro-4 : 5-dinitrobenzene and Certain of its Derivatives. JAN J. BLANKSMA (*Rec. trav. chim.*, 1902, 21, 419—423).—When nitrated, *o*-dichlorobenzene gives 1 : 2-dichloro-4 : 6-dinitrobenzene, and, in larger proportion, 1 : 2-*dichloro*-4 : 5-*dinitrobenzene*, which forms colourless leaflets melting at 110°; the latter is converted

by ammonia into 3 : 4-dichloro-6-nitroaniline, previously prepared by Beilstein and Kurbatow (Abstr., 1879, 309), and by methylamine into 3 : 4 *dichloro*-6-*nitromethylaniline*, which forms orange-red crystals melting at 148°. The corresponding 3 : 4-*dichloro*-6-*nitroethylaniline* melts at 120°. Fuming nitric acid converts the former substance into 3 : 4-*dichloro*-2 : 6-*dinitrophenylmethylnitroamine*, which forms colourless crystals melting at 121°.

3 : 4-*Dichloro*-6-*nitroanisole* results from the action of sodium methoxide on 1 : 2-dichloro-4 : 5-dinitrobenzene, and forms colourless crystals melting at 86°.

1 : 2-Dichloro-4 : 5-dinitrobenzene, when treated with sodium sulphide (compare Abstr., 1901, i, 461), gives a resinous oil, but with sodium disulphide 3 : 4 : 3′ : 4′-*tetrachloro*-6 : 6′-*dinitrodiphenyl disulphide* is obtained; this forms yellow crystals, and melts at 233°. 1-Bromo-3 : 4-dinitrobenzene with sodium sulphide gives a resin, but with the disulphide forms 3 : 3′-*dibromo*-2 : 2′-*dinitrodiphenyl disulphide*, melting at 184°, and yielding 5-bromo-2-nitrobenzenesulphonic acid when treated with fuming nitric acid. G. D. L.

Bromination and Nitration of Certain Derivatives of Benzylaniline. JAN J. BLANKSMA (*Rec. trav. chim.*, 1902, **21**, 428—431. Compare Abstr., 1902, i, 442, 600, and preceding abstracts).—*p*-Nitrobenzyl-*p*-nitroaniline (compare Paal and Benker, Abstr., 1899, i, 587), when treated with fuming nitric acid, gives 2 : 4 : 6-*trinitrophenyl*-p-*nitrobenzylnitroamine*, forming colourless crystals and melting and decomposing at 141°, and, when brominated, p-*nitrobenzyl*-2-*bromo*-4-*nitroaniline*, which forms greenish-yellow crystals and melts at 180°. Fuming nitric acid converts the latter compound into 2-*bromo*-4 : 6-*dinitrophenyl*-p-*nitrobenzylnitroamine*, which is obtained in colourless crystals melting at 132°.

p-Nitrobenzyl-*o*-nitroaniline, prepared by the action of *p*-nitrobenzyl chloride on *o*-nitroaniline, forms yellow crystals melting at 138° as stated by Bamberger (Abstr., 1894, i, 239), and not at 145° as stated by Paal and Benker (*loc. cit.*). On bromination, it gives, successively, p-*nitrobenzyl*-4-*bromo*-2-*nitroaniline*, forming yellow crystals melting at 151°, and p-*nitrobenzyl*-4 : 6-*dibromo*-2-*nitroaniline*, which forms yellow crystals and melts at 128°.

The corresponding *p*-nitrobenzyl-3-nitroaniline can be similarly nitrated and brominated with ease, but the products have not yet been investigated. G. D. L.

Behaviour of Thiocarbimides towards Magnesium-organic Compounds. FRANZ SACHS and HERMANN LOEVY (*Ber.*, 1903, **36**, 585—588).—Phenylthiocarbimide interacts with magnesium alkyl iodides to form thioanilides, which can be prepared in good yield by this method. Thioacetanilide was thus prepared from magnesium methiodide, whilst the ethiodide gave *thiopropionanilide*, NHPh·CSEt, which crystallises from dilute acetic acid in white, glistening needles, melts at 67—67·5°, and, like other compounds of the series, dissolves in dilute alkalis and is reprecipitated unchanged. Thiobenzanilide, NHPh·CSPh, prepared from phenylthiocarbimide and magnesium

phenyl bromide, melts at 101·5—102° and not at 97·5—98·5°. *Thiobutyranilide*, $NHPh \cdot CSPr^a$, crystallises from dilute acetic acid in white needles and melts at 32—33°. *Thioisovaleranilide*,

$$NHPh \cdot CS \cdot CH_2 \cdot CHMe_2,$$

crystallises in white needles (m. p. not given). *Thioisohexoanilide*, $NHPh \cdot CS \cdot CH_2 \cdot CH_2 \cdot CHMe_2$, forms white needles and melts at 63°.

T. M. L.

Condensation of Methylaniline with Acetaldehydecyanohydrin. FRANZ SACHS and WILLY KRAFT (*Ber.*, 1903, **36**, 757—763. Compare Abstr., 1902, i, 780).—A 65 per cent. yield of *methyl-a-cyanoethylaniline* (*a-methylanilinopropionitrile*), $NMePh \cdot CHMe \cdot CN$, obtained when monomethylaniline and acetaldehydecyanohydrin are heated with absolute alcohol for 2 hours at 100°, is a colourless liquid with a blue fluorescence, which distils at 147° under 20 mm. pressure and dissolves readily in most solvents. With concentrated sulphuric acid and a drop of dichromate solution, it yields an intense red coloration, and with alcoholic chloranil solution it gives the characteristic coloration for dialkylated-anilines. It yields a p-*nitroso*-derivative $NO \cdot C_6H_4 \cdot NMe \cdot CHMe \cdot CN$, crystallising in long, grass-green prisms and melting at 75·5°. The nitroso-compound condenses with an alcoholic solution of *p*-nitrobenzyl cyanide yielding the p-*methylcyanoethylaminophenylimide* of p-*nitrobenzoyl cyanide*,

$$NO_2 \cdot C_6H_4 \cdot C(CN){:}N \cdot C_6H_4 \cdot NMe \cdot CHMe \cdot CN,$$

which crystallises in well-developed, three-sided prisms with a bronzy lustre and melts at 142°. The nitroso-compound also condenses with phenylmethylpyrazolone yielding the *azomethine* derivative,

$$CN \cdot CHMe \cdot NMe \cdot C_6H_4 \cdot N{:}C{<}\begin{matrix} CO-NPh \\ CMe{:}N \end{matrix},$$

which crystallises in red needles melting at 190°.

a-Methylanilinopropionamide, $NMePh \cdot CHMe \cdot CO \cdot NH_2$, is formed when the corresponding nitrile is left in contact with concentrated sulphuric acid for 12 hours, then poured on to ice, and carefully rendered alkaline with ammonia; it crystallises in glistening needles, melts at 47·5°, and is readily soluble in most organic solvents and in dilute acids. It yields a p-*nitroso*-derivative crystallising in olive-green, six-sided prisms and melting at 159·5°.

The nitrosoamide condenses with benzyl cyanide yielding the *azomethine* compound, $CN \cdot CPh{:}N \cdot C_6H_4 \cdot NMe \cdot CHMe \cdot CO \cdot NH_2$, which crystallises in brick-red needles melting at 154°. With *p*-nitrobenzyl cyanide, it yields a similar *azomethine* derivative,

$$NO_2 \cdot C_6H_4 \cdot C(CN){:}N \cdot C_6H_4 \cdot NMe \cdot CHMe \cdot CO \cdot NH_2,$$

crystallising in dark violet plates and melting at 205—210°. With malononitrile, it forms the *methylcarbaminylethylaminophenylimide* of mesoxalonitrile, $C(CN)_2{:}N \cdot C_6H_4 \cdot NMe \cdot CHMe \cdot CO \cdot NH_2$, in the form of reddish-brown plates melting at 244·5°.

When the azomethine compound, derived from the nitrosoamide and benzyl cyanide, is hydrolysed and condensed with 2 : 4-dinitrobenzaldehyde, a *product*, $C_6H_3(NO_2)_2 \cdot CH{:}N \cdot C_6H_4 \cdot NMe \cdot CHMe \cdot CO \cdot NH_2$, is obtained melting at 235—238°.

J. J. S.

Preparation of ω-Cyanomethylaniline and its Derivatives. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 132621. Compare Abstr., 1898, i, 127).—Methyleneaniline and the corresponding derivatives of other aromatic amines yield cyanogen derivatives on treatment with hydrogen cyanide. To obtain the best yield, the base is converted into its sodium disulphite compound, and this is added to a solution of potassium cyanide and gently warmed. The cyano-derivative then separates. It is not necessary to isolate the disulphite compound, but the product of reaction of the base and sodium hydrogen sulphite may be employed directly.

ω-Cyanomethyl-p-*toluidine* and *ω-cyanomethylanthranilic acid* are white substances melting at 62° and 165° respectively. C. H. D.

New Di-iodophenol. P. BRENANS (*Compt. rend.*, 1903, 136, 236—238. Compare Abstr., 1901, i, 322, 643; 1902, i, 280, 673).—The hitherto unknown 3 : 5-di-iodophenol has been prepared, starting from 4 : 6-di-iodo-2-nitroaniline; the latter is converted into 3 : 5-di-iodonitrobenzene by diazotising with sodium nitrite in concentrated sulphuric acid and then adding to boiling alcohol. This di-iodonitrobenzene was obtained by Willgerodt and Arnold (Abstr., 1902, i, 16, 17) from 2 : 6-di-iodo-4-nitroaniline, but the substance thus prepared melted at 95—96°, whereas that obtained by the author melted at 103°. The yield of the nitrobenzene from the di-iodo-*o*-nitroaniline is more than twice that from the *p*-nitro-derivative. 3 : 5-Di-iodoaniline, prepared from the di-iodonitrobenzene, melted at 107°; Willgerodt and Arnold found the melting point to be 105°, and describe an acetyl derivative melting at 101—102°; the *acetyl* compound prepared by the author sublimed at 257—258° without melting and had the formula $C_6H_3I_2 \cdot NHAc$. The amino-group was replaced by the hydroxyl group in the usual manner, forming 3 : 5-*di-iodophenol*, $OH \cdot C_6H_3I_2$, which crystallises in colourless needles from water, melts at 103—104°, and is slowly volatile with steam. The *ethyl ether*, $OEt \cdot C_6H_3I_2$, crystallises in needles melting at 29—30° and is easily volatile with steam; the *acetate* forms colourless needles melting at 79°. K. J. P. O.

Preparation of the Dinitrophenols and Dinitroanisoles, and Certain of their Physical Properties. ARNOLD F. HOLLEMAN [with G. WILHELMY] (*Rec. trav. chim.*, 1902, 21, 432—447).—The method employed by the author for the separation of the mixture of 2 : 4- and 2 : 6-dinitrophenols, obtained on nitrating *o*-nitrophenol, differs from that of Hübner and Schneider (Abstr., 1873, 1030) in the fractional precipitation of the mixed potassium salts by barium chloride; the barium salt of 2 : 6-dinitrophenol being less soluble in water than that of the isomeric compound.

The separation of the mixture of 3 : 6-, 3 : 4-, and 2 : 3-dinitrophenols, obtained by the nitration of *m*-nitrophenol (compare Bantlin, Abstr., 1879, 237; and Henriques, Abstr., 1883, 327), is effected by taking advantage of the relatively sparing solubility of 3 : 6-dinitrophenol in alcohol and of 3 : 4-dinitrophenol in benzene. After separation by this means, the residue contains the 3 : 6- and 2 : 3-compounds, from

which the latter is separated by extraction with a little alcohol and purified by crystallisation from 25 per cent. acetic acid.

The ionisation constants of the isomeric dinitrophenols are given, and are sensibly in agreement with the measurements of Bader (Abstr., 1891, 257).

3 : 5-Dinitrophenol, the constant of which has not previously been measured, has K $2{\cdot}1 \times 10^{-7}$.

o-Nitrophenol and *p*-nitrophenol have K $6{\cdot}8 \times 10^{-8}$ and $6{\cdot}5 \times 10^{-8}$ respectively, and not $7{\cdot}5 \times 10^{-8}$ and $9{\cdot}6 \times 10^{-8}$, as given by Hantzsch (Abstr., 1900, i, 94), *m*-nitrophenol having K $1{\cdot}0 \times 10^{-8}$. The values of K for the dinitrophenols do not agree with the numbers calculated from those of phenol and the mononitrophenols by Ostwald's method.

2 : 4-Dinitroanisole is formed by treating 1-chloro-2 : 4-dinitrobenzene with potassium hydroxide in methyl-alcoholic solution, the 2 : 6-, 3 : 6-, 3 : 4-, and 2 : 3-isomerides being obtained from the silver salts of the corresponding phenols by means of methyl iodide (compare Salkowski, *Annalen*, 1874, **174**, 273 ; and Bantlin, *loc. cit.*). The 2 : 6-compounds may also be conveniently separated from the mixed 2 : 4- and 2 : 6-dinitroanisoles, obtained on nitrating *o*-nitroanisole, by extraction with carbon disulphide in quantity insufficient to secure complete solution and crystallisation of the extracted portion from alcohol in which the 2 : 6- is less soluble than the 2 : 4-compound.

The isomeric dinitroanisoles have the following sp. gr. in the fused state : 2 : 4, 1·3364 at 131·2°, 1·3596 at 108° ; 2 : 6, 1·3000 at 128·5°, 1·2906 at 138·7° ; 3 : 6, 1·3429 at 109·3°, 1·3233 at 127·5° ; 3 : 4, 1·3338 at 110·2°, 1·3138 at 130·5° ; 2 : 3, 1·3083 at 126·8°, 1·2990 at 137° ; 3 : 5, 1·3445 at 109°, 1·3222 at 130·4°. The corrected melting points, determined with 10 grams of material, are : 2 : 4, 86·9° ; 2 : 6 117·5° ; 3 : 6, 97° ; 3 : 4, 69 3° ; 2 : 3, 118·8° ; 3 : 5, 105·8°.

G. D. L.

Derivatives of Phenyl Ether. V. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1903, **25**, 60—68. Compare this vol., i, 163).—p-*Nitrophenyl* p-*tolyl ether*, $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4Me$, prepared by the action of *p*-bromonitrobenzene on potassium *p*-tolyloxide, melts at 66° and boils at 225° under 25 mm. pressure. On exposure to light, it speedily turns brown. Its *sulphonic acid* crystallises from water in light yellow needles melting at 102° ; the *barium* and *sodium* salts are described.

p-*Aminophenyl* p-*tolyl ether* melts at 122°. The *hydrochloride*, *hydrobromide*, *sulphate*, *nitrate*, and *platinichloride* were prepared.

When *p*-nitrophenyl *p*-tolyl ether is treated with nitric acid, a second nitro-group is introduced ; the product so obtained forms yellow needles melting at 101°. Corresponding nitro-derivatives, melting respectively at 98°, 100°, and 106°, were also produced from *o*-nitrophenyl *o*-tolyl ether, *o*-nitrophenyl *p*-tolyl ether, and *o*-nitrophenyl *m*-tolyl ether. When *p*-nitrophenyl *p*-tolyl ether is boiled with strong nitric acid, a *hexanitro*-derivative results.

The isomeric nitrophenyl tolyl ethers are contrasted. The closer the positions of the nitro- and methyl groups to one another, the greater is the tendency for the compound to be liquid. Spatial influence is also important in conditioning the stability of the amino-ethers, the most

stable variety being that where the amino- and the methyl groups are furthest apart.

o-Bromonitrobenzene acts more readily than its *p*-isomeride on potassium tolyloxides. A. McK.

Hydroxybenzyl Halides from Negatively Substituted Phenols. FARBENFABRIKEN VORM. FREDR. BAYER & Co. (D.R.-P. 132475).—The nitrophenols and halogen-phenols react with the halogen-methyl alcohols (or with formaldehyde and strong haloid acids) to form derivatives containing the group $-CH_2X$, where X = halogen. Phenols containing carboxyl or aldehyde groups react similarly (compare D.R.-P. 120374), but not phenolsulphonic acids. The presence of a dehydrating agent is necessary.

p-*Nitrohydroxybenzyl chloride*, obtained by passing gaseous hydrogen chloride into a solution of *p*-nitrophenol and formaldehyde in strong hydrochloric acid, separates as an oil crystallising in colourless needles melting at 132°, easily soluble in alcohol, benzene, acetic acid, and chloroform, less so in light petroleum and ether. The *iodide* melts at 169°.

o-*Nitrohydroxybenzyl chloride*, yellow needles, and melts at 75°; the corresponding *bromide* and *iodide* are yellow substances which melt at 76° and 112° respectively. o-*Chlorohydroxybenzyl chloride* crystallises from light petroleum in colourless needles melting at 112°; p-*chlorohydroxybenzyl chloride* melts at 85°. C. H. D.

Bromoxylenols. EMILIO NOETLING (*Ber*., 1903, 36, 656).—The compound described as 5-bromo-*m*-4-xylenol (Abstr., 1901, i, 588) is really the 6-bromo-derivative. J. J. S.

Iodine and Bromine Derivatives of Thymol. PAUL DANNENBERG (*Monatsh*., 1903, 24, 67—79).—On treating thymol with bromine (2 mols.), a yellow, oily compound is obtained which is soluble in alkali and therefore not a substitution product as supposed by Kehrmann (Abstr., 1890, 367). The o-*bromo*-p-*keto-bromide* crystallises at −14° and is analogous to the keto-bromides prepared by Zincke. On distillation in a vacuum, o-p-*dibromothymol* is formed; this is best prepared by the action of a mixture of sodium bromide and bromate on thymol. It boils at 186° under 20 mm. pressure and forms a *benzoate* melting at 80—81°.

The keto-iodides from thymol lose iodine very easily to form stable compounds, which are assumed to be bimolecular halogenides, that is, substituted quinones of diphenol. Similar products are obtained from mono- and dibromo-thymols. E. F. A.

New *o-cyclo*Hexanediol and its Derivatives. LÉON BRUNEL (*Compt. rend*., 1903, 136, 383—385. Compare this vol., i, 157).—o-cyclo*Hexanediol*, $C_6H_{10}(OH)_2$, is best prepared by heating iodo-*cyclo*hexanol with aqueous 15 per cent. potassium hydroxide under pressure, first at 75—80°, when the *eso*anhydride, $C_6H_{10}{:}O$, is formed, and then at 130—140°; it crystallises in colourless, orthorhombic

plates melting at 104° and boiling at 236° under 760 mm. pressure, when it becomes slightly brown. The *acetate* is a liquid; the *benzoate* crystallises in needles melting at 93·5°. The *monomethyl ether*, prepared from iodohexanol and silver oxide in the presence of 80 per cent. alcohol, is a colourless liquid boiling at 184—185° under 762 mm. pressure, and has a sp. gr. 0·9657 at 11·5°; the corresponding *ethyl ether* boils at 195° under 762 mm. pressure and has a sp. gr. 0·9467 at 11·2°.

The *cyclo*hexanediol (*o*-naphthene glycol) obtained by Markownikoff (Abstr., 1899, i, 22) by oxidising *cyclo*hexene by permanganate is not identical with the substance here described; Markownikoff's substance is to be called *α-o-cyclo*hexanediol, and the author's the *β*-compound.

K. J. P. O.

Coloured Substances Derived from Nitro-compounds. C. LORING JACKSON and R. B. EARLE (*Amer. Chem. J.*, 1903, **29**, 89—120. Compare Jackson and Gazzolo, Abstr., 1900, i, 433).—When a solution of trinitroanisole in benzene is treated with sodium *iso*amyloxide, an additive *compound* (*sodium dinitromethoxy*iso*amyloxyquinolnitrolate*), $C_5H_{11}\cdot O\cdot C_6H_2(NO_2)_2(OMe)\colon NO\cdot ONa$, is obtained as a bright red precipitate, which is decomposed by dilute hydrochloric acid with formation of *iso*amyl picrate and trinitroanisole. The same substance is produced when the additive compound with sodium methoxide is heated at 70° with *iso*amyl alcohol. By the action of aniline on the sodium methoxide compound, picrylaniline is produced, and by the action of hydroxylamine, picrylhydroxylamine is formed.

The compound, $C_6H_3(NO_2)_3,2CH_3\cdot ONa$ (sodium nitrodimethoxydiquinolnitrolate), obtained by the action of sodium methoxide on trinitrobenzene, is red and amorphous, and rapidly undergoes decomposition. If this compound is treated with dilute hydrochloric acid immediately after its preparation, it yields trinitrobenzene, but if left for 3 days in an exhausted desiccator and then treated with hydrochloric acid, no trinitrobenzene is produced, but tetranitroazoxybenzene is formed together with formaldehyde, nitrous acid, and other substances.

The additive *compound* of trinitroanisole (1 mol.) with sodium methoxide (2 mols.), $C_6H_2(NO_2)_3\cdot OMe,2CH_3\cdot ONa$ (*sodium nitrotrimethoxydiquinolnitrolate*), is an amorphous, orange-coloured powder which is freely soluble in water.

By the action of potassium cyanide on a solution of trinitroanisole in methyl alcohol, the *compound*, $C_6H_2(NO_2)_3\cdot OMe,2KCN$ (*potassium nitrodicyanodiquinolnitrolate*), is obtained as a reddish-brown, amorphous substance, freely soluble in water or alcohol and very unstable.

The *compound*, $C_6H_3(NO_2)_3,2C_6H_5\cdot ONa$ (*sodium nitrodiphenoxydiquinolnitrolate*), prepared by the addition of sodium phenoxide to an ethereal solution of trinitrobenzene, forms a brick-red, amorphous powder and is instantly decomposed by water.

The *compound*, $[C_6H_3(NO_2)_2\cdot SO_3]_2Ba,2CH_3\cdot ONa$ (*barium sodium nitrosulphomethoxyquinolnitrolate*), obtained by the action of sodium methoxide on barium dinitrobenzenesulphonate $[SO_3 : NO_2 : NO_2 =$

1 : 3 : 5], forms an amorphous, pale salmon-coloured powder and is soluble in water or ethyl alcohol. E. G.

Products of the Condensation of Saligenin with Aromatic Bases. CARL PAAL (*Arch. Pharm.*, 1902, **240**, 679—690. Compare Abstr., 1894, i, 450; 1895, i, 346; 1899, i, 748).—By heating saligenin (*o*-hydroxybenzyl alcohol) with an aromatic amine, NH_2R, at 150—160°, usually with a little alcohol and in a sealed tube, a product, $OH·C_6H_4·CH_2·NHR$, is prepared. A good yield is obtained when there is a substituting group in the para-position with regard to the amino-group; when there is a substituting group in the ortho-position, the yield is more or less diminished, and in some cases no definite product of condensation can be isolated (compare Abstr., 1899, i, 587). The action of acetic anhydride, in the cold, or after a short heating, on the product of condensation, converts it into a monoacetyl derivative, $OH·C_6H_4·CH_2·NAcR$; after boiling for some time, the diacetyl derivative, $OAc·C_6H_4·CH_2·NAcR$, is formed. A list of the compounds prepared is given below, with their melting points.

o-*Hydroxybenzyl*-p-*anisidine* [$R = C_6H_4·OMe(4)$], 128°; *monoacetyl* derivative, 98°; *diacetyl* derivative, crystalline. o-*Hydroxybenzyl*-p-*phenetidine* [$R = C_6H_4·OEt(4)$], 145—146°; *monoacetyl* derivative, 101°. o-*Hydroxybenzyl*-p-*chloroaniline* [$R = C_6H_4Cl(4)$], 121°; *monoacetyl* derivative, 95°; *diacetyl* derivative, glassy. o-*Hydroxybenzyl*-p-*bromoaniline* [$R = C_6H_4Br(4)$], 126°; *monoacetyl* derivative, 108°; *diacetyl* derivative, glassy.

With *o*-toluidine, no crystalline product could be obtained. o-*Hydroxybenzyl*-as-m-*xylidine* [$R = C_6H_3Me_2(2:4)$], 114°, small yield. With *p*-xylidine, only a very little crystalline product was obtained, and that not well crystallised. o-*Hydroxybenzyl-ψ-cumidine*

$$[R = C_6H_2Me_3(2:4:5)],$$

172—173°, yield about 50 per cent.; the *hydrochloride* was analysed. o-*Hydroxybenzyl*-o-*anisidine* [$R = C_6H_4·OMe(2)$], 70—71°, very small yield. o-*Hydroxybenzyl*-o-*chloroaniline* [$R = C_6H_4Cl(2)$], 118°, very small yield. With *o*-bromoaniline, very little crystalline product was obtained.

When saligenin is heated just to boiling with excess of methylaniline, some o-*hydroxybenzylaniline*, $OH·C_6H_4·CH_2·NMePh$, is obtained as an oil. C. F. B.

Benzyl Derivatives containing Sulphur, and their Decomposition by Dry Distillation. EMIL FROMM and OSCAR ACHERT (*Ber.*, 1903, **36**, 534—546).—When carefully purified benzyl sulphide is distilled under the ordinary pressure, either in an oil-bath or over a bare flame, it gives as sole products hydrogen sulphide, toluene, stilbene, thionessal (tetraphenylthiophen), and *s*-tetraphenylbutane; contrary to previous statements, carbon disulphide, sulphur, benzyl mercaptan, and dibenzyl are not produced, and the substance formerly described as "tolallyl sulphide" is really a mixture of stilbene, thionessal, and *s*-tetraphenylbutane, into which it can be resolved by crystallising it alternately from acetone and alcohol. Benzyl disulphide under similar circumstances gives the same products with the

addition of sulphur; the proportion of stilbene is smaller, and that of thionessal greater, than in the case of benzyl sulphide.

The first product of the decomposition of benzyl sulphide is undoubtedly stilbene, which is converted by the hydrogen sulphide simultaneously formed into thionessal, $2C_{14}H_{12} + H_2S = C_{28}H_{20}S + 6H$. It is the nascent hydrogen, formed according to the equation given, which reduces the stilbene to toluene and the thionessal to tetraphenylbutane, $C_{28}H_{20}S + 8H = C_{28}H_{26} + H_2S$. These changes were experimentally realised by the authors; it is, moreover, experimentally shown that neither stilbene nor thionessal is reduced by hydrogen sulphide to tetraphenylbutane according to the equations $2C_{14}H_{12} + H_2S = C_{28}H_{26} + S$ and $C_{28}H_{20}S + 3H_2S = C_{28}H_{26} + 4S$, so that the reducing agent is not hydrogen sulphide as such, but nascent hydrogen formed from it.

In the decomposition of benzyl disulphide, in addition to the foregoing changes, the sulphur initially formed converts the stilbene into thionessal, $2C_{14}H_{12} + S = C_{28}H_{20}S + 4H$, the nascent hydrogen produced reducing part of the stilbene to toluene.

Benzyl sulphoxide fails to give definite products with phenylhydrazine and hydroxylamine, but condenses wtih benzaldehyde giving a *compound*, $C_{21}H_{18}OS$, which crystallises from chloroform or acetone in small, white needles and melts at 203°. When distilled at 210°, benzyl sulphoxide is decomposed into sulphur dioxide, toluene, benzaldehyde, and benzyl disulphide; at 270°, the disulphide is further resolved in the manner already stated.

At 290°, benzylsulphone decomposes only partially, the principal products being sulphur dioxide, stilbene, and toluene.

s-*Tetraphenylbutane*, $CH_2Ph\cdot CHPh\cdot CHPh\cdot CH_2Ph$, prepared by reducing thionessal with tin and hydrochloric acid in alcoholic benzene solution, is very sparingly soluble in acetone and melts at 255°.

W. A. D.

p-**Dimethoxybenzhydrol.** Hans Schnackenberg and Roland Scholl (*Ber.*, 1903, 36, 654—655).—*p*-Dimethoxybenzophenone yields an oxime melting at 133° (compare Gattermann, Abstr., 1896, i, 173), which undergoes the Beckmann transformation, yielding *anisic anisidide*, $OMe\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, melting at 202°. The *phenylhydrazone*, $C(C_6H_4\cdot OMe)_2\colon N_2HPh$, melts at 123—124°. p-*Dimethoxybenzhydrol*, $CH(C_6H_4\cdot OMe)_2\cdot OH$, obtained by the reduction of the ketone by Zagumenny's method (this Journal, 1877, i, 459), crystallises from a mixture of ether and light petroleum, melts at 72°, and dissolves in concentrated acid yielding red solutions, but does not form solid salts. Its *acetyl* derivative melts at 83·5°. J. J. S.

Action of Zinc on Benzoyl Chloride. James F. Norris and D. R. Franklin (*Amer. Chem. J.*, 1903, 29, 141—149).—When benzoyl chloride is treated with zinc at the ordinary temperature, the quantities which interact are approximately those represented by the equation $2C_6H_5\cdot COCl + Zn = 2C_6H_5\cdot CO - + ZnCl_2$. The reaction is extremely complicated, and neither hydrogen chloride nor dibenzoyl is produced. When the experiment is carried out in presence of oxygen, only a small quantity of the gas is absorbed. The product of the reaction,

after removal of the zinc chloride, yields benzoic acid and a brown, amorphous substance melting at 125—130°. If the product is distilled, benzoic acid, benzoic anhydride, and a small, non-volatile residue are obtained. It was also observed that in some cases, when the product of the reaction was treated with water, zinc hydroxide was produced, the presence of an organo-metallic compound being thus indicated. E. G.

Constitution of van Heteren's Chloronitroethoxybenzonitrile. Jan J. Blanksma (*Rec. trav. chim.*, 1902, 21, 424—427. Compare van Heteren, Abstr., 1901, i. 460).—The chloronitromethoxy- (or ethoxy-) benzonitriles of van Heteren (*loc. cit.*) are converted by hydrolysis with concentrated hydrochloric acid into Meldola, Woolcott, and Wray's 4-chloro-3-nitrophenol (Trans., 1896, 69, 1322). The orientation of van Heteren's compounds is therefore $OR:CN:NO_2:Cl = 6:1:2:3$.

When nitrated, the ethoxy-compound gives 3-*chloro*-2 : 5-*dinitro*-6-*ethoxybenzonitrile*, which forms yellow crystals melting at 65°; this, when treated with alcoholic ammonia, yields 3-*chloro*-5-*nitro*-2-*amino*-6-*ethoxybenzonitrile*, which forms yellow crystals and melts at 157°, whilst by the action of sodium monosulphide (whereby the nitro-group in position 2 is eliminated) a sulphide is obtained which forms yellow crystals and melts at 146°. G. D. L.

Esterification of Unsymmetrical Di- and Poly-basic Acids. IX. Esterification of Sulphonic and Sulphocarboxylic Acids. Rudolf Wegscheider and Margarethe Furcht (*Monatsh.*, 1902, 23, 1093—1146. Compare Abstr., 1900, i, 657; 1901, i, 32; 1902, i, 617—620).—Methyl benzenesulphonate cannot be prepared by the action of methyl alcohol on the acid or of methyl iodide on the sodium salt in presence of methyl alcohol, but is formed by the action of methyl sulphate on the acid (compare Krafft and Roos, Abstr., 1892, 1219; 1894, i, 91; Kastle and Murrill, Abstr., 1895, i, 370). It boils at 154° under 20 mm. pressure; it forms a 1/55 normal aqueous solution, and has at 25°, with a concentration of 1 gram mol. per litre, the hydrolysis constants, with water, K 0·0006; with normal potassium hydroxide solution, K 0·051; and with normal hydrochloric acid, K 0·0024. The corresponding constants for methyl benzoate are, with potassium hydroxide, K 2·4; with hydrochloric acid, K 0·00004.

Methyl m-*sulphobenzoate*, formed by the action of methyl sulphate on the acid, crystallises in large, hard prisms, melts at 32—33°, boils at 198—200° under 20 mm. pressure, and is easily soluble in alcohol, ether, or benzene, but almost insoluble in water (compare Limpricht and von Uslar, *Annalen*, 1857, 102, 252; 1858, 106, 30). The β-monomethyl ester is formed by the action of methyl alcohol on the acid, of methyl alcohol and hydrogen chloride on the sodium hydrogen salt, of methyl iodide on the silver salt in presence of methyl alcohol, of methyl alcohol on m-sulphobenzoic semichloride, and on hydrolysis of the dimethyl ester with methyl alcohol or water. It forms a syrup which crystallises in a vacuum, melts at 65—67°, is

extremely hygroscopic, is easily soluble in water or alcohol, but only slightly so in ether or benzene. On exposure to moist air, hydrolysis takes place. The α-monomethyl ester, [$CO_2H : SO_3Me$], formed by the action of methyl iodide on the silver salt, melts at 139—140°, is not hygroscopic, and is easily soluble in alcohol, ether, or hot benzene, but almost insoluble in water; when distilled in a vacuum, both monomethyl esters are partially converted into the dimethyl ester and the acid.

On addition of concentrated sodium chloride solution to an aqueous solution of the β-monomethyl ester, the sodium salt is precipitated. *m*-Sulphobenzoic semichloride crystallises from benzene and melts at 133—134°. The constitution is uncertain; the formation of the β-monomethyl ester points to [$COCl : SO_3H$], but the solubility in benzene and insolubility in water to [$CO_2H : SO_2Cl$].

The action of methyl alcohol on *m*-sulphobenzoyl chloride,

[$COCl : SO_2Cl$],

leads to the formation of the β-monomethyl ester and an *ester chloride*, [$CO_2Me : SO_2Cl$], which melts at 63—65°, is moderately stable, only slightly hygroscopic, and is easily soluble in benzene or ether.

Dimethyl p-*sulphobenzoate*, formed by the action of methyl sulphate on the acid, crystallises in white leaflets, melts at 88—90°, and is easily soluble in benzene or ether, less so in alcohol, and insoluble in water; it is also formed by the action of methyl iodide on the *silver* salt, $C_7H_4O_5SAg_2$, crystallises from water in white nodules, and is easily decomposed by light. The *α-monomethyl* ester,

[$CO_2H : SO_3Me$],

formed by the action of methyl iodide on the silver hydrogen salt, separates from ether in small, white crystals, melts at 195—196°, and is easily soluble in hot ether. *Silver hydrogen* p-*sulphobenzoate*, $C_7H_5O_5SAg,1\frac{1}{2}H_2O$, forms large, transparent crystals, is easily soluble in cold water, loses water on exposure to air, and is stable to light. The *β-monomethyl* ester, [$CO_2Me : SO_3H$], formed by the same methods as the corresponding meta-ester, is obtained as a light yellow syrup, which solidifies over phosphorus pentoxide, melts at 99—100°, is easily soluble in water and alcohol, and yields a *silver* salt, $C_8H_{17}O_5SAg$, and a *sodium* salt. *Sodium hydrogen* p-*sulphobenzoate*, obtained on addition of sodium chloride to the aqueous solution of the acid, forms glistening crystals and does not react with methyl iodide at 150°.

The esters of *o*-nitro-*p*-sulphobenzoic acid are formed by the same reactions as the esters of the sulphobenzoic acids. The *dimethyl* ester crystallises from water in white prisms, melts at 86—87°, is easily soluble in ether, and is hydrolysed to the β-monomethyl ester when boiled with alcohol. The *β-monomethyl* ester, [$CO_2Me : SO_3H$], melts at 95—97°, is very hygroscopic, and is easily soluble in water or alcohol. The *α-monomethyl* ester melts at 140—142° and is easily soluble in ether or hot benzene, but almost insoluble in water. G. Y.

Preparation of Salicylic Acid. Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 133500).—In the preparation of salicylic acid by the action of carbon dioxide on sodium phenoxide, the pro-

duct of the fusion of an alkali benzenesulphonate with an alkali hydroxide, consisting of phenoxide and alkali sulphite, may be substituted for the pure phenoxide. Oxidation and darkening in colour is thus hindered, and alkali economised. C. H. D.

Synthesis of Anisic and of *p*-Ethoxybenzoic Acids. F. Bodroux (*Compt. rend.*, 1903, **136**, 377—379).—Bromophenyl alkyl ethers react readily with magnesium in dry ethereal solution forming organo-magnesium compounds, resembling in all respects the corresponding alkyl magnesium compounds; aldehydes, ketones, esters, iodine, and bromine act on them violently; with water, the original phenyl ether is regenerated. Carbon dioxide is absorbed, forming a phenyl magnesium carbonate, thus:

$$OR\cdot C_6H_4\cdot MgBr + CO_2 = OR\cdot C_6H_4\cdot CO_2\cdot MgBr,$$

which, on treatment with an acid, is converted into a substituted benzoic acid. Anisic acid can be obtained from *p*-bromoanisole by heating magnesium with an ethereal solution of the anisole until the whole of the magnesium is dissolved, then passing in dry carbon dioxide and treating the mixture immediately with hydrochloric acid. *p*-Ethoxybenzoic acid was prepared in a similar manner from phenetole.
K. J. P. O.

Condensation of Benzaldehyde with Hydroxy-acids. Josef Mayrhofer and Karl Nemeth (*Monatsh.*, 1903, **24**, 80—86).—Benzaldehyde and malic acid are condensed by heating with piperidine at 150—160°, forming a compound crystallising in white plates and melting at 116°. This is β-benzoylpropionic acid, as it forms a *syn*-oxime melting at 129° and convertible into the *anti*oxime melting at 96° (compare Dollfus, Abstr., 1892, 1202).

From the condensation of benzaldehyde and citric acid a compound, $C_{20}H_{18}O_8$, melting at 143—144° has been isolated. This forms an *ester* boiling at 195° under 12 mm. pressure, and a *diacetyl* derivative melting at 104°, and is probably a condensation product of aconitic acid with 2 mols. of benzaldehyde, thus:

$$OH\cdot CHPh\cdot CH(CO_2H)\cdot C(CO_2H){:}C(CO_2H)\cdot CHPh\cdot OH.$$

E. F. A.

Absorption Spectra of Indigotin, Diaminoindigotin, and Tetra-azoindigotin. Josef M. Eder (*Monatsh.*, 1903, **24**, 13—18).—Measurements of the extinction and absorption coefficients by Vierordt's method. Indigotin shows a narrow band in the yellow with a maximum at $\lambda = 615$ $\mu\mu$. Diaminoindigotin has a narrow absorption band in the orange-red, which increases in the direction of green and blue for solutions of greater concentration, and has its maximum at $\lambda = 623$ $\mu\mu$, the change produced by the amino-groups being thus about 8 $\mu\mu$ towards the red. Tetra-azoindigotin shows a strong band with a maximum at $\lambda = 565$ $\mu\mu$ in the yellow, and a small band in the green with a maximum at $\lambda = 517$ $\mu\mu$. E. F. A.

Preparation of Bromo-derivatives of Indigotin. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 132266).—The *dibromoindoxyl* obtained on treating indoxyl with bromine water is substituted in both the benzene and the pyrrole nuclei (compare this vol., i, 32). On heating with sodium acetate, or, better, with aniline or pyridine, hydrogen bromide is eliminated and a symmetrical p-*dibromoindigotin* formed. By passing oxygen into an alkaline solution of indoxyl and bromoindoxyl, monobromoindigotin is formed. C. H. D.

Condensation of Phthalic Anhydride with Halogen Derivatives of Benzene. CARL GRAEBE, WILLIAM THÉVENAZ, and KNEELAND (*Arch. Sci. phys. nat.*, 1903, [iv], 15, 232).—The three dichlorobenzenes and bromobenzene do not condense with phthalic anhydride in the presence of aluminium chloride. Chlorobenzene affords small quantities of chlorobenzoylbenzoic acid, and condensation, yielding fluorobenzoylbenzoic acid, occurs with greater ease when fluorobenzene is employed. G. D. L.

Nitromethane and Phthalic Anhydride. SIEGMUND GABRIEL (*Ber.*, 1903, 36, 570—579).—When to a solution of phthalic anhydride and nitromethane in ether at 0° sodium methoxide is added, the principal product is methyl phthalate, but a small quantity of a substance probably having the constitution $NO_2\cdot CH_2\cdot C(OH){<}{\overset{O}{\underset{C_6H_4}{}}}{>}CO$, is also formed; on heating with acetic anhydride, the latter is converted into *nitromethylenephthalide*, $NO_2\cdot CH{:}C{<}{\overset{O}{\underset{C_6H_4}{}}}{>}CO$, which crystallises from glacial acetic acid, sinters at 205°, melts and decomposes at 206—208°, and is converted by boiling hydriodic acid in presence of phosphorus into *iso*coumarin. With cold aqueous potassium hydroxide, the phthalide gives ω-*nitroacetophenone*-o-*carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot CH_2\cdot NO_2,$$

which crystallises from water in colourless leaflets, melts at 121·5°, and yields a *silver* salt, $CO_2Ag\cdot C_6H_4\cdot CO\cdot CH{:}NO_2Ag$; when heated with concentrated hydrochloric acid at 100°, the acid is resolved into hydroxylamine and phthalonic acid.

With methyl-alcoholic potassium hydroxide at 0°, nitromethylenephthalide gives the *additive* compound,

$$NO_2K{:}CH\cdot C(OMe){<}{\overset{O}{\underset{C_6H_4}{}}}{>}CO,$$

which crystallises in white needles and is decomposed by dilute hydrochloric acid forming α-*methoxy*-α-*nitromethylphthalide*,

$$NO_2\cdot CH_2\cdot C(OMe){<}{\overset{O}{\underset{C_6H_4}{}}}{>}CO;$$

this crystallises from boiling water in flat needles, melts at 110—111°, and on warming with aqueous potassium hydroxide at 60° is converted into ω-nitroacetophenone-*o*-carboxylic acid (*supra*).

When reduced by stannous chloride, ω-nitroacetophenone-*o*-carboxylic acid gives a *base*, $C_9H_7O_3N$, which crystallises from water in bright rose-coloured, soft needles, and when heated in a capillary tube above

160° forms a scarlet deposit on the sides of the tube; it yields a *hydrochloride*, which loses hydrogen chloride at 100°, and probably is a 2 : 4-*dihydroxyisocarbostyril* formed as follows:

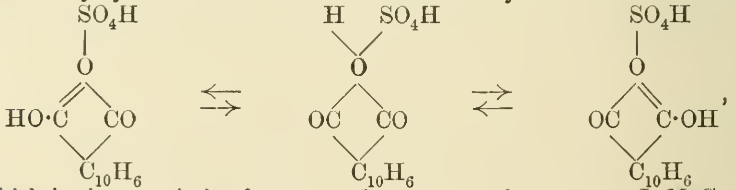
$$CO_2H\cdot C_6H_4\cdot CO\cdot CH_2\cdot NO_2 \rightarrow CO_2H\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH\cdot OH \rightarrow C_6H_4 {<}\begin{matrix} CO\cdot CH_2 \\ CO\cdot N\cdot OH \end{matrix} + H_2O.$$

The nitromethylenephthalide described is shown not to be identical with Zincke's substance of the same name (Abstr., 1892, 1231).

W. A. D.

Fluorescence of Naphthalic Anhydride. JOHN T. HEWITT (*J. Soc. Chem. Ind.*, 1903, **22**, 127—128).—The author calls attention to the theory of fluorescence developed by him (Proc., 1900, **16**, 3), and discusses Francesconi and Bargellini's results (this vol., i, 34) on the fluorescence of substituted derivatives of naphthalic anhydride.

Naphthalic anhydride in benzene or acetic acid solution shows no fluorescence, but in concentrated sulphuric acid a blue, fluorescent solution is obtained. This may be due to the formation of an oxonium salt which it has not yet been possible to isolate, and which may show the doubly symmetrical tautomerism indicated by the formulæ:



which is characteristic of so many fluorescent substances. J. McC.

Methylgallic Acids. [Gallic Acid Methyl Ethers.] CARL GRAEBE (*Ber.*, 1903, **36**, 660).—Some of the compounds recently described (this vol., i, 262) have already been prepared by Herzig and Pollak (*ibid.*, i, 89). J. J. S.

Alkyl Derivatives of Gallic Acid, Pyrogallolcarboxylic Acid, and Pyrogallol. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1903, **36**, 660—662. Compare this vol., i, 89; and also Graebe and Martz, *ibid.*, i, 262, and preceding abstract).—*Methyl 2-hydroxy-3 : 4-dimethoxybenzene-1-carboxylic acid*, $OH\cdot C_6H_2(OMe)_2\cdot CO_2Me$, obtained by the action of diazomethane on methyl pyrogallolcarboxylate, melts at 75—78° and is only sparingly soluble in alcohol. The corresponding *acid*, $OH\cdot C_6H_2(OMe)_2\cdot CO_2H$, melts at 169—172°, and when heated at 200° yields 2 : 3-*dimethoxyphenol* distilling at 122—123° under 17 mm. pressure, and at 232—234° under atmospheric pressure. J. J. S.

Derivatives of *m*-Acetylaminobenzaldehyde. PAUL FRIEDLÄNDER and R. FRITSCH (*Monatsh.*, 1903, **24**, 1—12).—m-*Acetylaminobenzaldehyde*, prepared by the acetylation of *m*-aminobenzaldehyde, crystallises with difficulty from benzene in small, white plates melting at 84°, and forms an *oxime* melting at 185°. When nitrated in the cold with a mixture of fuming nitric and strong sulphuric acids in glacial acetic acid solution, a nearly quantitative transformation into

6-*nitro-3-acetylaminobenzaldehyde* is brought about. This crystallises in brown needles melting at 161° and yields a *phenylhydrazone* melting at 247°, and an *oxime* which melts at 189°. When exposed for some time in benzene solution to sunlight, a yellowish-white precipitate is formed; this dissolves unchanged in soda, and its acetic acid solution showed the green colour characteristic of nitroso-compounds; it is probably 6-*nitroso-3-acetylaminobenzoic acid*; when heated, it decomposes at 240°. Nitroacetylaminobenzaldehyde dissolves easily in cold moderately concentrated sodium hydroxide; after a time, or more quickly on heating, brilliant red-brown crystals separate of 6-*nitro*-3-*amino-benzaldehyde*, which crystallises from water in yellow needles and gives a *phenylhydrazone* melting at 212°.

6-*Nitro-3-acetylaminophenyllactyl methyl ketone*,

$$NO_2 \cdot C_6H_3(NHAc) \cdot CH(OH) \cdot CH_2 \cdot COMe,$$

formed by dissolving nitroacetylaminobenzaldehyde in acetone and careful treatment in the cold with barium hydroxide, crystallises with $2H_2O$ in colourless needles melting at 62°. The anhydrous compound melts at 142°. On further action of the alkali, or more quickly on warming, *diacetyldiaminoindigotin* is formed, which is easily hydrolysed on heating at 120—130° with dilute mineral acids to *diaminoindigotin*. The last two compounds were not obtained in a sufficiently pure state for analysis. E. F. A.

p-Ethylbenzaldehyde. H. Fournier (*Compt. rend.*, 1903, 136, 557—558).—*p*-Ethylbenzaldehyde could not be prepared by Gattermann's method from ethylbenzene, carbon monoxide, and hydrogen chloride in the presence of aluminium chloride. On treating ethylbenzene with the acid chloride of monoethyl oxalate in the presence of aluminium chloride, *ethyl* p-*ethylphenylglyoxylate*, $C_6H_4Et \cdot CO \cdot CO_2Et$, is formed; it is a colourless liquid boiling at 186—188° under 30 mm. pressure; the corresponding *acid* crystallises well and melts at 70—71°, and when heated with concentrated sulphuric acid is converted into *p*-ethylbenzoic acid (m. p. 113°). When heated with aniline, *ethylbenzylideneaniline*, $C_6H_4Et \cdot CH \colon NPh$, is produced; it melts at 2—3° and boils at 208—210° under 20 mm. pressure; the corresponding *toluidine* derivative melts at 49°. When boiled with dilute sulphuric acid, both these substances are converted into p-*ethylbenzaldehyde*, a colourless liquid boiling at 221° and oxidised slowly by the air to *p*-ethylbenzoic acid; the *hydrazone* forms yellow needles melting at 101°; the *semicarbazone* melts at 199° and the *oxime* at 29°.

On oxidising *p*-ethylmethylbenzene with manganese dioxide and sulphuric acid (compare Abstr., 1902, i, 15), this aldehyde is formed in small amount together with *p*-tolualdehyde; methyl *p*-tolyl ketone is, however, the main product of the oxidation. K. J. P. O.

Aldoximation of Anisole by means of Mercury Fulminate and Aluminium Oxychloride. Roland Scholl and J. Hilgers (*Ber.*, 1903, 36, 648—650. Compare Abstr., 1900, i, 144, and this vol., i, 254).—A mixture of *o*- and *p*-anisaldoximes, anisonitrile, and anisaldehyde is obtained when anisole is left in contact with mercuric

fulminate, anhydrous aluminium chloride, hydrated aluminium chloride, and aluminium hydroxide at 40—45°, and the mixture then poured on to ice and concentrated hydrochloric acid. A small amount of a *compound*, $C_{15}H_{16}O_3$,HCl, forming red crystals is obtained as a by-product.
J. J. S.

Aldoximation of Phenetole by means of Mercury Fulminate and Aluminium Oxychloride. ROLAND SCHOLL and A. KREMPER (*Ber.*, 1903, 36, 650—654).—Phenetole, when treated in a similar manner to anisole (compare preceding abstract), yields *p*-ethoxybenzaldoxime, *p*-ethoxybenzaldehyde, *p*-ethoxybenzonitrile, and a *compound*, $C_{17}H_{20}O_3$, which yields a *hydrochloride* in the form of red crystals melting at 103°.
J. J. S.

Abnormal Course of the Michael Condensation. ARTHUR MICHAEL (*Ber.*, 1903, 36, 763).—The so-called ketopentamethylene derivative, obtained by Svodoba (this vol., i, 174), has been previously shown by the author to be a ketotetramethylene compound (Abstr., 1901, i, 125).
J. J. S.

Acetophenone and Other Ketones in Coal Tar. RUDOLF WEISSGERBER (*Ber.*, 1903, 36, 754—757).—Acetophenone was isolated from heavy oil boiling between 160° and 190° and previously freed from acids and bases, by taking advantage of its solubility as a feeble base in sulphuric acid of 60° B. (compare Baeyer and Villiger, Abstr., 1901, i, 658; 1902, i, 112 and 355); the acid solution was distilled with steam, the oil obtained, after drying, heated with phenylhydrazine for 3—4 hours at 100°, and the unattacked oil removed by steaming. The phenylhydrazone left was decomposed by hydrochloric acid, and a ketonic oil boiling between 145° and 210° obtained; from a fraction of this boiling between 190° and 210°, acetophenone was isolated in the form of its *p*-bromophenylhydrazone.
W. A. D.

Preparation and Properties of Two Tetra-alkyldiaminodiphenylanthrones. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1903, 136, 535—537. Compare Abstr., 1901, i, 350).—*Tetramethyldiaminodiphenylanthrone*, $CO<\substack{C_6H_4 \\ C_6H_4}>C(C_6H_4\cdot NMe_2)_2$, is readily prepared by condensing the chloride of anthraquinone with dimethylaniline in the presence of aluminium chloride, using carbon disulphide as solvent (compare Tétry, Abstr., 1899, i, 818); it crystallises in yellow plates melting at 278° and with 1 mol. of benzene in yellow needles having the same melting point, and dissolves in acids forming well-crystallised, colourless salts; it reacts neither with phenylhydrazine nor hydroxylamine. *Tetraethyldiaminodiphenylanthrone* is also prepared with ease in a similar manner, and crystallises in slender, yellow needles melting at 218°; its salts with mineral acids are colourless and well defined.
K. J. P. O.

Preparation of Ionone. HAARMANN & REIMER (D.R.-P. 132222, 133145, and 133563).—Acids having oxidising properties, such as nitric and chromic acids, may be employed to convert ψ-ionone into ionone. As when other dilute acids are employed, the product is a mixture of the α- and β-isomerides (compare Abstr., 1894, i, 82).

Acetylionone is converted by a solution of barium hydroxide or dilute acids into ionone, the product consisting chiefly of the β-compound.

α-Ionone is obtained almost exclusively when ψ-ionone is mixed with concentrated formic acid (compare Abstr., 1902, i, 342, 471).

C. H. D.

Syntheses in the Naphthacenequinone Series. I. CHR. DEICHLER and CH. WEIZMANN (*Ber.*, 1903, 36, 547—560).—1-*Hydroxynaphthacenequinone*, $C_6H_4<\begin{matrix}CO\cdot C\cdot C(OH)\\ CO\cdot \overset{||}{C}\text{——}CH\end{matrix}>C_6H_4$, obtained by heating a mixture of phthalic acid, α-naphthol, and boric acid with 97 per cent. sulphuric acid at 160—165° for an hour, forms reddish-yellow needles, melts at 303°, and gives an *acetyl* derivative, which crystallises from benzene in yellowish needles.

The structure of the compound follows from its giving naphthacene on distillation with zinc dust, dihydronaphthacene on reduction with hydriodic acid (b. p. 127°) at 170°, and the dihydroxynaphthacenequinone, $C_6H_4<\begin{matrix}CO\cdot C\cdot C(OH)\\ CO\cdot \overset{||}{C}\cdot C(OH)\end{matrix}>C_6H_4$ (Gabriel and Leupold, Abstr., 1898, i, 482), on fusion with an alkali hydroxide.

If in the preceding preparation 92 per cent. sulphuric acid is used and the temperature kept at 130° for 2 hours, the principal product (30 per cent. of the whole) is *o*-1-*hydroxynaphthoylbenzoic acid*, $OH\cdot C_{10}H_6\cdot CO\cdot C_6H_4\cdot CO_2H$; this substance is formed in quantity corresponding with 76 per cent. of the theoretical on fusing phthalic anhydride and α-naphthol with boric acid alone at 170—190° for 1 hour, and crystallises from benzene, melts at 186—187°, and gives a *sodium* salt which forms large, bright yellow leaflets. The *acetyl* derivative crystallises from methyl alcohol in nearly colourless crystals and melts at 190°. The *methyl* ester separates from alcohol in yellow crystals, melts at 108—109°, and the *ethyl* ester is similar and melts at 91°. The structure of the acid follows from its formation together with α-naphthol when α-naphthafluorane, the configuration of which is known (Meyer, Abstr., 1893, i, 275), is fused with potassium hydroxide at 150—160° for 6 hours.

Attempts to prepare 1-hydroxynaphthoylbenzoic acid by substituting sodium acetate or phosphoric acid for boric acid give unfavourable results; but if boric acid be used, hydroxy- and sulphophthalic acids can be employed in place of phthalic acid. β-Naphthol, however, cannot be substituted for α-naphthol.

In preparing α-hydroxynaphthacenequinone, it is advantageous to prepare the hydroxynaphthoylbenzoic acid by using boric acid alone and then to heat this with sulphuric acid, which eliminates water.

W. A. D.

Syntheses in the Naphthacenequinone Series. II. CHR. DEICHLER and CH. WEIZMANN (*Ber.*, 1903, 36, 719—728. Compare preceding abstract).—*Hydroxynaphthacenequinonesulphonic acid*,

$$C_6H_4<\begin{matrix}CO\cdot C\text{——}C(OH)\\ \quad\;\, \| \\ CO\cdot C\cdot C(SO_3H?)\end{matrix}>C_6H_4,$$

prepared by heating hydroxynaphthoylbenzoic acid with 20 times its weight of sulphuric monohydrate containing 5 per cent. of boric acid for 2 hours at 170—190°, crystallises from water in orange-yellow leaflets, gives sparingly soluble alkali salts, and, when fused with potassium hydroxide, yields the dihydroxynaphthacenequinone,

$$C_6H_4<\begin{matrix}CO\cdot C\cdot C(OH)\\ \quad\;\, \| \\ CO\cdot C\cdot C(OH)\end{matrix}>C_6H_4;$$

the latter fact, however, does not definitely determine the structure of the sulphonic acid, since small quantities of hydroxynaphthacenequinone are also formed, and this, when fused with alkali, can be converted into the dihydroxy-compound.

The foregoing dihydroxynaphthacenequinone, identical with the substance described by Gabriel and Leupold (Abstr., 1898, i, 482), is also produced by heating hydroxynaphthacenequinone with 10 times its weight of 96 per cent. sulphuric acid containing 10 per cent. of boric acid for 3—4 hours at 230°; but as the product is not uniform, the dihydroxy-compound is obtained more readily by fusing the monohydroxy-derivative with potassium hydroxide and a little potassium chlorate for 12 hours at 165—170°, or by oxidising it with sulphuric acid and sodium nitrite. The corresponding *diacetoxynaphthacenequinone* crystallises from benzene or glacial acetic acid in bright yellow needles and melts at 235°.

Dihydroxynaphthacenequinonesulphonic acid,

$$C_6H_4<\begin{matrix}CO\cdot C\cdot C(OH)\\ \quad\;\, \| \\ CO\cdot C\cdot C(OH)\end{matrix}>C_6H_3\cdot SO_3H,$$

is prepared by heating 15 grams of hydroxynaphthoylbenzoic acid or hydroxynaphthacenequinone with 200 grams of sulphuric acid of sp. gr. 1·84, containing 15 grams of boric acid for 1 hour at 140°, then adding 220 grams of 25 per cent. sulphuric anhydride, heating for 2 hours at 180°, and finally raising the temperature to 250° for 4—5 hours; it crystallises from water or dilute acetic acid in red leaflets, gives a sparingly soluble, bluish-violet *potassium* salt, and is converted by fusion with potassium hydroxide at 170° into a *trihydroxynaphthacenequinone*, $C_6H_4<\begin{matrix}CO\cdot C\cdot C(OH)\\ \quad\;\, \| \\ CO\cdot C\cdot C(OH)\end{matrix}>C_6H_3\cdot OH$. This crystallises from nitrobenzene in small, coffee-brown leaflets and dissolves in alkalis giving ruby-red solutions, which rapidly become colourless owing to atmospheric oxidation. An isomeric *trihydroxynaphthacenequinone* is obtained by heating naphthacenediquinone (Gabriel and Leupold, *loc. cit.*) with 25 per cent. sulphuric anhydride for 5 hours at 100°; it crystallises from nitrobenzene in violet needles, melts at 300° (uncorr.), and dissolves in alkalis with a bluish-violet coloration. W. A. D.

Derivatives of Menthol. IVAN KONDAKOFF and JULIUS SCHINDELMEISER (*J. pr. Chem.*, 1903, [ii], 67, 193—196. Compare Abstr., 1895, i, 549, and Zelinsky, Abstr., 1902, i, 185).—Menthyl bromide,

prepared by the action of phosphorus pentabromide on menthol at the ordinary temperature, boils at 100—103° under 13 mm., at 104—106° under 15 mm. pressure, and has a sp. gr. 1·163 at 20°, $[\alpha]_D$ − 9·68° at 20°, and n_D 1·48602 at 20°. If the reacting mixture is cooled, the menthyl bromide boils at 103—105° under 13 mm. pressure and has a sp. gr. 1·159 at 20°, $[\alpha]_D$ + 18·33° at 20°, and n_D 1·48602 at 20°. When boiled with alcoholic potassium hydroxide, the latter menthyl bromide is partly converted into menthene, which boils at 166—168° under 758 mm. pressure and has a sp. gr. 0·815, $[\alpha]_D$ − 80·22°, and n_D 1·45369 at 20°. The remainder of the bromide yields two fractions; one, containing traces of menthene, boils at 100—103° under 14 mm. pressure and has a sp. gr. 1·062, $[\alpha]_D$ + 36·71°, and n_D 1·47702 at 20°; the other boils at 103—106° under 15 mm. pressure and has a sp. gr. 1·140, $[\alpha]_D$ + 42·54°, and n_D 1·48496 at 20°. *ter.*-Menthol, formed from the menthene by Reychler's process (Abstr., 1897, i, 246), is obtained in two fractions: the first boils at 80—91° under 13 mm. pressure, and yields a menthene, which boils at 172—178° under 762 mm. pressure and has a sp. gr. 0·816 and $[\alpha]_D$ − 66·20° at 20°; the second fraction is optically inactive; tertiary menthol boils at 91—93° under 13 mm., at 206—207° under the ordinary pressure, has a sp. gr. 0·900 and n_D 1·46188 at 20°, and is converted by concentrated hydrochloric acid into optically inactive menthyl bromide, which boils at 98—99° under 11 mm. pressure and has a sp. gr. 1·165 and n_D 1·48718 at 20°. When heated with alcoholic potassium hydroxide, this bromide yields an optically inactive menthene, which boils at 169—176° and has a sp. gr. 0·815 and n_D 1·45429. When acted on by fuming hydrobromic acid for one month at 5°, and then for three months at 20—22°, menthol yields a menthyl bromide which boils at 101—106° under 12 mm. pressure, has a sp. gr. 1·138, $[\alpha]_D$ + 41·38°, and n_D 1·48467 at 20°, and is converted by boiling alcoholic potassium hydroxide partly into menthene. The residual bromide boils at 100—101° under 11 mm. pressure and has a sp. gr. 1·105, $[\alpha]_D$ + 54°29′, and n_D 1·48554 at 20°. The menthene boils at 166·5—169°, has a sp. gr. 0·812, $[\alpha]_D$ − 85·38°, and n_D 1·45509, and is converted by Reychler's process partly into tertiary menthol. The residual menthene boils at 171—177° and has a sp. gr. 0·816 and $[\alpha]_D$ − 83·21° at 20°. G. Y.

Substituted Aminoacetates of Menthol and Borneol. ALFRED EINHORN and STEPHAN JAHN (*Arch. Pharm.*, 1902, 240, 644—651).—*Menthyl* and *bornyl chloroacetates*, $CH_2Cl\cdot CO_2R$ ($R = C_{10}H_{19}$ or $C_{10}H_{17}$), were prepared by heating menthol and borneol respectively with chloroacetic acid and some strong sulphuric acid; the first boils at 240—270° and melts at 38°, the second boils at 147° under 30 mm. pressure. When allowed to remain with diethylamine at the ordinary temperature, they form respectively *menthyl* and *bornyl diethylaminoacetates*, $NEt_2\cdot CH_2\cdot CO_2R$, which boil under 20 mm. pressure at 160—162° and 160° respectively; the *methiodides* of these melt at 157° and 194°, the *methochlorides*, which crystallise with $1H_2O$, at 185° and 130°; the *hydrochloride* of the first melts at 108°, the *citrate* of the second at 146°. With aminocamphor at 80°, the two chloroacetates condense to *menthyl* and *bornyl camphorylaminoacetates*, $C_{10}H_{15}O\cdot NH\cdot CH_2\cdot CO_2R$, respectively; the *hydrochlorides* of these melt at 208° and 237°, the

nitrate and *sulphate* of the second at 186° and 142° respectively; in the preparation of the latter, some dihydrodicamphenepyrazine (Duden and Pritzkow, Abstr., 1899, i, 779) is obtained as a by-product.

Menthyl diethylaminoacetate hydrochloride is readily soluble in water, and decomposes in living organisms with elimination of menthol; hence, it should form a useful drug. C. F. B.

Rotatory Power of the Homologous Esters of Borneol, *iso*-Borneol, and Camphocarboxylic Acid. JULES MINGUIN and E. GRÉGOIRE DE BOLLEMONT (*Compt. rend.*, 1903, **136**, 238—240. Compare Abstr., 1902, i, 383).—With the object of testing Tschugaeff's rule (Abstr., 1898, i, 274, 495; 1899, ii, 3), which states that the mol. rotatory power of a homologous series does not vary from member to member, a number of esters of borneol, *iso*borneol, and camphocarboxylic acid have been investigated.

Bornyl stearate shows the limiting value for the rotatory power of the homologous series of the esters of the fatty acids, namely, 4°10′ in benzene solution and 4°30′ in alcoholic solution. A double linking, as instanced by the rotatory power of the oleate and crotonate, has no great influence; the same holds for the cinnamate.

*iso*Bornyl esters appear not to follow the rule, but it is found that the *iso*borneol has been partly changed into *i*-camphene, which then forms inactive esters with the acids. The rotations are less in benzene solution.

In the case of the esters of camphocarboxylic acid, the rotation is not comparable with that of the bornyl esters, because in the preparation of the esters, isomerides are formed.

In these experiments, solutions containing 0·25 gram-mol. per litre were used, and a 25 cm. tube was employed. The table gives a summary of the results and the boiling points of the esters:

	$[\alpha]_D$ in alcoholic solution.	$[\alpha]_D$ in benzene solution.	Boiling point.	$[\alpha]_D$ of regenerated *iso*borneol.
Bornyl stearate	—	−4°10′	—	—
,, oleate	−4°14′	−4 10	295° at 18 mm.	—
,, crotonate	−4 44	−4 10	173 ,, 19 ,,	—
,, cinnamate	−5 2	−4 10	melts at 33°	—
*iso*Bornyl formate	−3 10	—	103° at 16 mm.	−24° 3′
,, acetate	−4 14	—	106 ,, 14 ,,	−24 3
,, propionate	−5 8	−4°45′	150 ,, 13 ,,	−28
,, *iso*butyrate	−5 20	−4 53	120 ,, 14 ,,	−28
,, butyrate	−5 40	−5 6	123 ,, 11 ,,	−29 2
,, valerate	−5 56	−5 28	136 ,, 12 ,,	−31 27
,, laurate	−6	−5 34	202 ,, 30 ,,	−32
Methyl camphocarboxylate	+6 10	—	162 ,, 16 ,,	—
Ethyl ,,	+6 30	—	164 ,, 20 ,,	—
Propyl ,,	+6 38	—	170 ,, 19 ,,	—
*iso*Butyl ,,	+7 14	—	177 ,, 19 ,,	—
Allyl ,,	+7 6	—	160—170° at 20 mm.	—

K. J. P. O.

Oxides of the Terpene Series. Friedrich W. Semmler (*Ber.*, 1903, 36, 764—770).—The compound, $C_{10}H_{16}O$, described by Wallach as a ketone (Abstr., 1894, i, 44), is shown to be an *oxide*, and is termed *dihydrocarvoxide*. Its constitutional formula is probably $CH\left\langle\begin{array}{c} CMe{=}CH{-}O \\ CH_2 \\ CH_2{\cdot}CH_2{\cdot}CHMe \end{array}\right\rangle CH$. It yields a *dibromide* melting at 55°, which readily decomposes yielding hydrogen bromide. Permanganate converts the oxide into Tiemann and Semmler's hydroxy-ketone, $C_9H_{16}O_2$, melting at 58—59° (Abstr., 1895, i, 674). An alcoholic solution of hydroxylamine reacts with the oxide yielding a base, $CH\left\langle\begin{array}{c} CHMe{\cdot}CH(NH{\cdot}OH){\cdot}O \\ CH_2 \\ CH_2{-}CH_2{-}CHMe \end{array}\right\rangle CH$, melting at 113—114°. Its *benzoyl derivative*, $C_{17}H_{23}O_3N$, melts at 144° and does not combine with bromine. The *hydrochloride* of the base, $C_{10}H_{19}O_2N,HCl$, is insoluble in ether and melts at 93°.

Alcoholic potash at 160° decomposes the base, yielding ammonia and a monobasic *hydroxy-acid*, $C_{10}H_{18}O_3$. Its *urethane* melts at 227°; its *silver* salt is relatively stable. On oxidation, a *ketonic acid*, $C_{10}H_{16}O_3$, is obtained which yields a *semicarbazone* melting at 178—179°. Bromine water under pressure converts the hydroxy-acid into *iso-cuminic acid*, $CO_2H{\cdot}CHMe{\cdot}C\left\langle\begin{array}{c} CH{\cdot}CH \\ CH{:}CH \end{array}\right\rangle CMe$.

J. J. S.

Fenchene. Iwan L. Kondakoff (*J. pr. Chem.*, 1903, [ii], 67, 94—111).—Polemical. An answer to Wallach (Abstr., 1902, i, 685) with reference to the priority of the discovery of the isomeric transformation of secondary hydroaromatic alcohols.

E. F. A.

Sesquiterpenes and Sesquiterpene-Alcohols. Johannes Gadamer and T. Amenomiya (*Arch. Pharm.*, 1903, 241, 22—47. Compare Ueno, *J. Pharm. Soc. Japan*, No. 129, 1074).—Atractylol is obtained by distilling the roots of the Japanese plant *Atractylis ovata* (order *Compositæ*) with steam. After recrystallisation from solutions in light petroleum or alcohol, cooled by means of solid carbon dioxide and ether, it melts at 59°, boils at 290—292° under 760 mm. and at 162° under 15 mm. pressure, is optically inactive, and has n_D 1·511 at 20°. It has the composition, $C_{15}H_{26}O$, of a sesquiterpene-alcohol, but it hardly gives the derivatives that an alcohol should, as it loses water very readily with formation of the sesquiterpene. Phenylcarbimide forms no phenylcarbamate, but abstracts water from it, forming carbon dioxide and diphenylcarbamide. Hydrogen chloride or bromide, when passed into an ethereal solution of the alcohol, does not merely replace the OH by halogen, X, but also combines additively, forming an unstable compound of the type $C_{15}H_{26}X_2$. With phosphorous tri-iodide in carbon disulphide solution, an oily product with the composition $C_{15}H_{25}I$ was obtained, but it decomposed readily into two liquids, the upper mobile one being presumably the

hydrocarbon $C_{15}H_{24}$, the lower viscid one, the compound $C_{15}H_{26}I_2$. Nitric acid gave no definite product; certainly no nitrate was formed. Neither with acetic acid nor with a pyridine solution of acetic anhydride (Verley and Bölsing, Abstr., 1901, i, 54) did it form an acetyl derivative; it reacted, however, to the extent of about 50 per cent. when boiled with acetic anhydride and dehydrated sodium acetate, but the product decomposed to a large extent when distilled. With benzoyl chloride in pyridine solution, it formed a benzoyl derivative to the extent of about 30 per cent., but this, again, was not stable when distilled. The alcohol was not oxidised by chromic acid mixture or potassium permanganate. All its reactions point to its being a tertiary alcohol.

Atractylene, $C_{15}H_{24}$, the sesquiterpene formed from atractylol by elimination of water, is best obtained by heating atractylol with potassium hydrogen sulphate at 180°. It boils at 260—261° under the ordinary pressure, at 125—126° under 10 mm., has a sp. gr. 0·9101 at 20°/15°, and n_D 1·5089 at 20°, the last corresponding with the presence of two double linkings. It readily polymerises, getting more viscid, and changing its odour from that of cedar-wood to that of lemons. When prepared from the dihydrochloride (obtained from atractylol and hydrogen chloride) by heating this with aniline on the water-bath, it has the sp. gr. 0·9267 at 20°/4° and n_D 1·5056 at 20°; the last corresponds with one double linking, and the substance is probably already polymerised. With hydrogen iodide in ethereal solution, it seems to give the same product as was obtained with atractylol. It only takes up two atoms of bromine in carbon tetrachloride solution, the product being an oil. It was not found to be converted into atractylol (by taking up water) when it was heated with sulphuric acid and water in the presence of much acetic acid (Abstr., 1893, i, 101). The nitrosochloride and nitrosate could only be obtained as unstable oils.

Experiments were also made with caryophyllene, patchouli-alcohol, (guaiol tiglic aldehyde, champacol), and oil of *Carlina acaulis*, but no new results of importance seem to have been obtained. C. F. B.

Ethereal Oil of Calamintha Nepeta, called "Marjolaine" in the South of France. PAUL GENVRESSE and E. CHABLAY (*Compt. rend.*, 1903, 136, 387—389).—Schimmel's "Marjolaine" is extracted from *Origanum Majorana*, and Tombarel's from *Calamintha Nepeta.* The oil from the source last mentioned, separated by distilling in steam, soon becomes yellow, has a sp. gr. 0·904 at 16°, and a_D 18°39′ at 15° in chloroform solution. On fractional distillation, *l*-pinene, a new ketone, calaminthone, and pulegone, were isolated. *Calaminthone*, $C_{10}H_{16}O$, obtained in a pure state from its oxime, is a colourless liquid boiling at 208—209° under 745 mm. pressure, has a sp. gr. 0·930 at 20°, a_D 11°10′ at 21° in chloroform solution, and a mol. refraction 45·385; it forms an additive compound with bromine. The *oxime* crystallises in white needles melting at 88—89° and has a_D − 6°7′; its *hydrochloride* melts at 165°. The *semicarbazone* forms yellow crystals melting at 165°. On reduction, the ketone is converted into menthol. K. J. P. O.

Peppermint Oil from Piedmont. CARLO EDOARDO ZAY (*Chem. Centr.*, 1903, i, 331—332; from *Staz. sperim. agrar. ital.*, 35, 816—823).—An examination of three 1901 Italian peppermint oils gave the following data. The first is described as extra refined, whilst the two last are crude oils. The oils had respectively sp. gr. at 15°, 0·916, 0·9171, 0·9256; acid number, 0·18, 0·76, 2·03; saponification number, 45·2, 30·0, 33·7; ether number, 45·0, 29·2, 21·6; iodine number, 147·1, 125·2, 131·9; n_D at 16°, 1·468, 1·467, 1·468; rotatory power (100 mm. tube), −2·34°, −10·41°, −7·4°; $[\alpha]_D$ at 16,° −2·55°, −11·4°, −7·9°; and contained 45·78, 51·5, 38·99 per cent. of free menthol, and 9·72, 7·10, 6·01 of combined menthol. The original paper also contains a description of the physical properties of the oils and their behaviour towards acetic anhydride, Tollen's reagent, &c. Adulteration of the refined oil with American turpentine may be readily recognised by the iodine number, by the polarimetric rotation, and by the behaviour of the oil with potassium iodide in Marpmann's test (*Pharm. Zeit.*, 1893, 466).

E. W. W.

Mecca Balsam. EDUARD HIRSCHSOHN (*Chem. Centr.*, 1903, i, 459—460; from *Pharm. Centr.-Halle*, 44, 33—35).—The behaviour of three samples of Mecca balsam of 1891—1895 and three of previous years towards various solvents and reagents has been investigated. All the samples were found to contain castor oil, and hence were probably prepared by digesting the plant or the resin with this oil. One sample appeared to contain Canada balsam, and another to be identical with Chios turpentine.

E. W. W.

Two New Glucotannoids. EUGÈNE GILSON (*Compt. rend.*, 1903, 136, 385—387).—Two new glucotannoids, glucogallin and tetrarin, have been obtained from Chinese rhubarb. *Glucogallin*, $C_{13}H_{16}O_{10}$, forms colourless or pale yellow crystals melting and decomposing at about 200° and soluble with a brownish-red coloration in potassium hydroxide, with a brownish-yellow coloration in sodium carbonate, and with a rose-red coloration in ammonia. With ferric salts, it gives a blue-black, and with potassium cyanide a pale rose, coloration. With both normal and basic lead acetates and with tartar emetic, the aqueous solution gives precipitates, but not with gelatin or proteids. Glucogallin differs from gallic acid by its insolubility in ether. By dilute sulphuric acid, it is decomposed into mol. proportions of gallic acid and *d*-dextrose.

Tetrarin, $C_{32}H_{32}O_{12}$, crystallises in colourless, transparent plates melting and decomposing at about 204—205°, and is soluble in alkali hydroxides and ammonia. By acids, it is decomposed into dextrose, gallic acid, cinnamic acid, and rheosmin.

Rheosmin, $C_{10}H_{12}O_2$, crystallises in rhombic needles melting at 79·5° and is soluble in alkali hydroxides, but is reprecipitated by carbon dioxide; it has all the properties of an aldehyde, reducing ammoniacal silver oxide, giving a crystalline compound with sodium hydrogen

sulphite, and an oxime with hydroxylamine, and resinifying under certain conditions.

Besides glucogallin and tetrarin, a catechin was isolated from the rhubarb. K. J. P. O.

Aloins of Natal Aloes. Eugène Léger. (*J. Pharm. Chim.*, 1903, [vii], 17, 13—17. Compare Abstr., 1902, i, 685).—The composition and properties of nataloin are best expressed by the formula $C_{23}H_{26}O_{10}$; it is sparingly soluble in water and ether, soluble in ethyl acetate, alkali hydroxides, ammonia, and pyridine, and in concentrated hydrochloric and hydrobromic acids. *Tetrabenzoylnataloin* is amorphous, yellow, and insoluble in water, soluble in alcohol and ether; *hexabenzoylnataloin* forms yellow, non-crystalline grains, soluble in ether, sparingly so in cold alcohol. Sodium peroxide gives *nataloemodin methyl ether*, which forms pale orange-yellow needles melting at 238°, and gives violet and orange-red colorations with concentrated sulphuric acid and sodium hydroxide respectively. On distillation with zinc dust, methylnataloemodin gives a methylanthracene, and on heating at 170° with concentrated hydrochloric acid, *nataloemodin*, which forms long, orange-red needles melting at 220·5°, and giving a red coloration with concentrated sulphuric acid and a violet with sodium hydroxide.

Homonataloin closely resembles nataloin, forming similar tetra- and hexa-benzoyl derivatives. Both homologues give a green colour with concentrated sulphuric acid and manganese dioxide or potassium dichromate and a violet colour on addition of ammonium persulphate to their solutions in sodium hydroxide. The latter colouring matter dyes silk, but not mordanted cotton. G. D. L.

Constitution of the Aloins. Eugène Léger (*J. Pharm. Chim.*, 1903, [vii], 17, 52—55. Compare Abstr., 1902, i, 685).—The two nataloins are regarded as condensation compounds of trihydroxymethylanthraquinone and a pentose, the latter group being apparently less stably attached than in other aloins. These two aloins, on treatment with nitric acid, give oxalic and picric acids, and not nitrohydroxyanthraquinones like barbaloin.

The differences between the barbaloins and the isomeric frangulin are explained by assigning to the latter a structure

$$C_{15}H_7O_2(OH)_2\cdot O\cdot CH{<}\begin{matrix}CH\cdot[CH\cdot OH]_3\cdot CH_3\\ |\\ O\end{matrix}$$

(compare barbaloin, *loc. cit.*).

G. D. L.

Constituents of Cathartic Drugs. O. A. Oesterle (*Chem. Centr.*, 1903, i, 297; from *Schweiz. Woch. Pharm.*, 40, 600—602).—By the action of chromic acid on aloemodin in presence of glacial acetic acid, a compound is formed which appears to be identical with Tschirch and Heuberger's rhein (this vol., i, 107); it crystallises from pyridine in reddish-yellow needles, melts at 314°, and is insoluble in chloroform.

This compound was also isolated from the alochrysin residues (Abstr., 1899, i, 538) containing aloxanthin (Tilden, Abstr., 1897, ii, 266). The acetyl derivative crystallises from glacial acetic acid in yellow needles and melts at 240°; the somewhat darker diacetyl derivative melts at 263°. E. W. W.

Polymerisation and Fission of the Molecule in the Pyranol Series. ROBERT FOSSE (*Compt. rend.*, 1903, **136**, 379—381).—It has previously been shown that naphthyloldinaphthapyran (the *eso*anhydride of 2 : 2′ : 2″-trihydroxy-1 : 1′ : 1″-trinaphthylmethane; Abstr., 1902, i, 449) breaks up into bromonaphthol and dinaphthapyryloxonium bromide, $CH\lessgtr\begin{smallmatrix}C_{10}H_6\\C_{10}H_6\end{smallmatrix}\gtr O\cdot Br$; in a similar manner, bisdinaphthapyryl (the *eso*anhydride of *s*-2 : 2′ : 2″ : 2‴-tetrahydroxy-1 : 1′ : 1″ : 1‴-tetranaphthylethane), $O<\begin{smallmatrix}C_{10}H_6\\C_{10}H_6\end{smallmatrix}>CH\cdot CH<\begin{smallmatrix}C_{10}H_6\\C_{10}H_6\end{smallmatrix}>O$, yields 2 mols. of dinaphthapyryloxonium bromide. Bisdinaphthapyryl is prepared by heating a solution of dinaphthapyryloxonium bromide with a small quantity of zinc dust in glacial acetic acid solution, and crystallises in prisms melting and decomposing at about 300°; when heated with mol. proportions of bromine in solution of carbon disulphide, it is reconverted into the oxonium salt. As previously stated, bisdinaphthapyryl is also formed by treatment of dinaphthapyranol,

$$OH\cdot CH<\begin{smallmatrix}C_{10}H_6\\C_{10}H_6\end{smallmatrix}>O$$

(this vol., i, 49), with zinc dust. K. J. P. O.

Constitution of Nencki and Sieber's "Resacetein," $C_{16}H_{12}O_4$. CARL BÜLOW (*Ber.*, 1903, **36**, 730—736).—The properties of "resacetein" (Abstr., 1881, 811) point to its being 7-*hydroxy*-2-op-*dihydroxyphenyl*-4-*methylene*-1 : 4-*benzopyranol*,

$$OH\cdot C_6H_4<\begin{smallmatrix}O\text{———————}\\C(:CH_2)\cdot CH\end{smallmatrix}>C\cdot C_6H_3(OH)_2,$$

formed by the loss of $2H_2O$ between 2 mols. of resacetophenone; it is best prepared by boiling resorcinol with glacial acetic acid and anhydrous zinc chloride for 2 hours at 158—160°, and gives a *picrate*, $C_{16}H_{12}O_4,C_6H_3O_7N_3,H_2O$, which crystallises in reddish-brown needles. When slowly distilled with aqueous sodium hydroxide, it is resolved into resorcinol and resacetophenone.

Similar pyranol derivatives are obtained by heating phenol or orcinol with acetic anhydride and zinc chloride. W. A. D.

Alkaloids of Isopyrum and Isopyroine. GEORGE B. FRANKFORTER (*J. Amer. Chem. Soc.*, 1903, **25**, 99—102).—From the roots of *Isopyrum biternatum*, *isopyroine hydrochloride*, melting at 255—257°, was prepared. The *platinichloride* melts at 238°. *Isopyroine*, $C_{28}H_{46}O_9N$, crystallises from alcohol and melts at 160°; it is not identical with the isopyrine or the ψ-isopyrine of Hartsen (this Journal, 1873, 511). The *methiodide* was also prepared. A. McK.

Action of Nitrous and of Hydrochloric Acids on Papaverine. AMÉ PICTET and G. H. KRAMERS (*Arch. Sci. phys. nat.*, 1903, [iv], **15**, 121—131).—By the action of sodium nitrite on papaverine hydrochloride, papaveraldoxime is formed.

When nitrous fumes are led into a boiling solution of papaverine hydrochloride in chloroform, *nitrosopapaverine nitrite* is produced, and forms straw-yellow prisms melting and decomposing at 179°. *Nitrosopapaverine* melts at 181·5°, forms colourless, silky needles, becoming green on exposure to light, and does not give Liebermann's reaction.

Of the salts of nitrosopapaverine, the hydrochloride, nitrate, and platinichloride melt and decompose at 181°, 183°, and 235° respectively; the picrate melts at 120°.

On boiling papaverine with an excess of concentrated hydrochloric acid, *dimethylpapaveroline*, $C_{16}H_9N(OMe)_2(OH)_2$, is obtained as a colourless substance, soluble in alcohol, sparingly so in ether, and insoluble in light petroleum, giving a greenish-yellow colour with ferric chloride and reducing ammoniacal silver solutions. The free compound undergoes oxidation by air with great ease, resinifying and becoming green, probably on account of the two hydroxy-groups being in the ortho-position. The *picrate* forms yellow needles melting at 104°; the *platinichloride* is colourless and amorphous.

By heating papaverine hydrochloride at 195—200°, methyl chloride is set free and *trimethylpapaveroline* is obtained; it crystallises in colourless tablets, decomposes without fusion at 240°, is sparingly soluble in cold alcohol or chloroform, almost insoluble in benzene, light petroleum, or ether, does not give a coloration with concentrated sulphuric acid or sulphuric acid containing ferric chloride, but yields a red tint with Mandelin's reagent. The *hydrochloride* separates from water in a hydrated form melting at 65°, whilst the anhydrous salt melts at 192°. The *platinichloride* is orange-yellow and melts and decomposes at 231°; the *mercurichloride* forms colourless needles melting and decomposing (in the anhydrous state) at 155°; the *picrate* forms yellow tablets melting at 206·5°; the sodium derivative melts between 160° and 175°. The *methiodide* and *methochloride* both crystallise in tetrahedra, melting at 63—64° and 70—71° respectively. On reduction of the methochloride with tin and hydrochloric acid, a base, iso*laudanine*, isomeric with laudanine and having many similar properties, is obtained; it melts at 76° and differs further from laudanine in developing blue colorations with sulphuric acid containing ferric chloride and with Fröhde's and Lafon's reagents, each of which gives a red colour with laudanine.

G. D. L.

Preparation of ψ-Tropine. EMANUEL MERCK (D.R.-P. 133564).—Tropidine may be largely converted into ψ-tropine by the action of hydrolytic agents on its hydrogen haloid additive compounds at a high temperature.

The compounds used as a starting point are obtained by heating tropidine with haloid acids in closed vessels.

Hydriodotropidine hydriodide crystallises from hot water in four-sided tables melting with decomposition at 197°, the free *hydriodotropidine*

is a heavy, colourless oil, soluble in water, *hydrobromotropidine* is also an oil, boiling at 109° under 17 mm. pressure.

Dilute acids or solutions of salts may be employed as hydrolytic agents, the reacting substances being heated together in closed vessels at 180—220°. Some tropidine is regenerated at the same time by elimination of the hydrogen haloids, but this may be removed by distillation in a current of steam. C. H. D.

Syntheses in the Tropine Group. IV. Monocyclic Alkamines of the Tropine Group and a Second Synthesis of Tropidine. RICHARD WILLSTÄTTER (*Annalen*, 1903, 326, 1—22).—Attempts have been made to synthesise tropine, $\begin{array}{lll} CH_2\cdot CH & — & CH_2 \\ | & NMe & CH\cdot OH \\ CH_2\cdot CH & — & CH_2 \end{array}$, from the synthetic methyltropidine (dimethylamino-$\Delta^{2:4}$-*cyclo*heptadiene), $\begin{array}{l} CH_2\cdot CH(NMe_2)\cdot CH \\ CH_2—CH{:}CH—CH \end{array}$, by forming an additive product with hydrogen chloride, $\begin{array}{l} CH_2\cdot CH(NMe_2)\cdot CH_2 \\ CH_2—CH{:}CH—CHCl \end{array}$, which, on treatment with aqueous sodium carbonate, yields ψ-methyltropine (ψ-dimethylamino-Δ^4-*cyclo*heptenol), $\begin{array}{l} CH_2\cdot CH(NMe_2)\cdot CH_2 \\ CH_2—CH{:}CH—CH\cdot OH \end{array}$. The latter forms a dibromo-additive product which, as free base, undergoes an isomeric change into the quaternary 2-bromotropinemethylammonium bromide (the methobromide of 2-bromotropanol),

$$\begin{array}{l} CH_2—CH(NMe_2)—CH_2 \\ CH_2\cdot CHBr\cdot CHBr\cdot CH\cdot OH \end{array} \longrightarrow \begin{array}{lll} CH_2\cdot CH & — & CH_2 \\ | & NMe_2Br & CH\cdot OH \\ CH_2\cdot CH & — & CHBr \end{array}.$$

Although, on reduction with zinc dust and hydriodic acid, the tropan ring is not affected, the compound is not converted into tropine, but water and bromine are eliminated, a tropidine methiodide being formed, $\begin{array}{lll} CH_2\cdot CH & — & CH_2 \\ | & NMe_2I & CH \\ CH_2\cdot CH & — & CH \end{array}$, which can be converted into tropidine by the removal of methyl iodide. These reactions afford a second complete synthesis of this base from suberone (*cyclo*heptone) (compare Abstr., 1901, i, 225).

Methyltropine (3-dimethylamino-Δ^4-*cyclo*heptenol),

$$\begin{array}{l} CH_2\cdot CH(NMe_2)\cdot CH_2 \\ CH_2—CH{:}CH—CH\cdot OH \end{array}$$

(compare Merling, Abstr., 1882, 216; and Ladenburg, *ibid.*, 670), boils at 247—248° (corr.) under the ordinary pressure and at 130—131° under 12—12·5 mm.; the *platinichloride* melts and decomposes at 161°, and the *aurichloride* melts at 96°; this base is easily converted by warming with benzoic anhydride in benzene solution into a *benzoyl* derivative, the *hydrochloride* of which crystallises in clusters of slender prisms or needles melting at 171—172°. The *hydrobromide* of methyltropine dibromide, prepared from methyltropine hydrobromide and bromine

water, crystallises in prisms or plates melting and decomposing at 178°. The free base changes into the isomeric 2-*bromotropinemethylammonium bromide*, which is best prepared by adding a chloroform solution of bromine to a solution of methyltropine in aqueous hydrobromic acid; the mixture is now made alkaline with sodium carbonate, and the chloroform layer, which contains the methyl ammonium bromide, separated; the latter crystallises in lustrous leaflets or needles melting and decomposing at 233°. The corresponding *iodide*, $C_8H_{14}ONBr{\cdot}MeI$, crystallises in prisms or needles less soluble in water than the bromide, and melting and decomposing at 233—234°. On reduction by most agents, the tropan ring is broken and methyltropine is formed; with zinc dust and hydriodic acid, tropidine methiodide is produced (see above).

A detailed account of the conversion of ψ-methyltropine (synthesised from methyltropidine or dimethylamino-$\Delta^{2:4}$-*cyclo*heptadiene) into the corresponding 2-bromo-ψ-tropinmethylammonium bromide is given (compare Abstr., 1901, i, 225). The *hydrochloride* of the benzoyl derivative of ψ-methyltropine crystallises in four-sided plates or short prisms melting at 166—167°. 2-*Bromo-ψ-tropinemethylammonium iodide*,

$$\begin{array}{l} CH_2{-}CH{-\!\!-\!\!-}CHBr \\ |\quad\;\; NMe_2I\;\; CH{\cdot}OH \\ CH_2{-}CH{-\!\!-\!\!-}CH_2 \end{array}$$

crystallises in four-sided plates or short prisms melting and decomposing at 238°.

1-*Methylamino*-Δ^4-cyclo*heptene*-3-*ol*, $\begin{array}{l} CH_2{\cdot}CH(NHMe){\cdot}CH_2 \\ CH_2{-\!\!-\!\!-}CH{:}CH{\cdot}CH{\cdot}OH \end{array}$, has been prepared by forming the additive product of hydrogen chloride and methylamino*cyclo*heptadiene and replacing the chlorine by hydroxyl by means of sodium hydrogen carbonate; an oily mixture of two isomerides is obtained, from which one separates in crystals; when pure, the latter forms prisms melting at 103—104° and absorbs moisture and carbon dioxide. It forms an additive product with bromine, which, however, differs from the corresponding derivatives of methyltropine and methyl-ψ-tropine in not yielding a dicyclic tropan derivative; on reduction of this additive product, an isomeride of methylamino*cyclo*heptenol melting at 127—129° is obtained. K. J. P. O.

Synthesis of Tropine. Richard Willstätter (*Annalen*, 1903, 326, 23—42. Compare preceding abstract).—Since the author demonstrated that ψ-tropine could be obtained from tropidine (Abstr., 1901, i, 744) and that ψ-tropine can be oxidised to tropinone, which can then be reduced to tropine (Abstr., 1900, i, 404), Ladenburg has also prepared tropine from tropidine by use of the author's method (Abstr., 1902, i, 390, 639), as the means formerly employed by him to effect this change (Abstr., 1890, i, 1167, 1333) were not free from objection.

With hydrogen iodide, tropidine hydriodide forms an additive product, 3-iodotropan hydriodide, melting and decomposing at 197°, which is identical with the compound obtained by the action of red phosphorus and hydriodic acid on tropine (Ladenburg, Abstr., 1883, 670). Tropidine hydrobromide does not form the additive product,

3-bromotropane hydrobromide, with hydrogen bromide in the cold, but only at 50°. 3-Bromotropane, $\begin{array}{l} CH_2\cdot CH—CH_2 \\ \vert \quad\;\; NMe \;\; CHBr \\ CH_2\cdot CH—CH_2 \end{array}$, prepared by the action of alkalis on the additive product, is an insoluble oil boiling at 109—109·5° under 17·5 mm. pressure and having a sp. gr. 1·3682 at 15·75°/4° (compare van Son, Abstr., 1898, i, 282, and 1899, i, 311); the *platinichloride* crystallises in thin prisms melting and decomposing at 210—211°, the *aurichloride* in prisms melting at 157—158°. The *methiodide* forms aggregates of sparingly soluble prisms and is converted on reduction into Δ^3-methyltropan; the *methobromide* crystallises in prisms or leaflets; the *platinichloride* obtained from it crystallises in long, orange-red prisms melting and decomposing at 247—248°.

A detailed account of the conversion of 3-bromotropan into ψ-tropine is given (compare Abstr., 1901, i, 744); the yield of ψ-tropine amounts to 24 per cent. of the theoretical.

A comparison has been made between the behaviour of tropine and that of ψ-tropine; when distilled in steam, tropine is slowly volatilised, whilst pure ψ-tropine is non-volatile. From a mixture of tropine and its stereoisomeride, ψ-tropine can be isolated by this means in a pure state, but with considerable loss, as some of the ψ-tropine distils with the tropine. As has been previously shown, a complete separation can be effected by means of the picrate (Abstr., 1900, i, 404); Ladenburg's statement (Abstr., 1902, i, 390) that such is not the case being incorrect. K. J. P. O.

Synthesis of r-Cocaine. Richard Willstätter and Adolf Bode (*Annalen*, 1903, **326**, 42—78).—The main points of this paper have been published (Abstr., 1901, i, 482); in this communication, the subject is dealt with in greater detail, and the crystallographic characters of ecgonine (*d*, *l*, and *r*) and its salts and of *r*-cocaine are given. The hydrochloride of *r*-cocaine crystallises in rhombic plates or leaflets melting and decomposing at 205—205·5°; the nitrate forms oblong leaflets or plates melting and decomposing at 172°. The *aurichloride* crystallises with $2H_2O$ and melts at 65—70° when hydrated, and at 164—165° when anhydrous. All attempts to decompose *r*-cocaine into the *d*- and *l*- forms by means of its salts with active acids (malic, quinic, camphoric, and tartaric acids) were unsuccessful. K. J. P. O.

Oxidation of 2 : 4-Dimethylpyrrole. Giuseppe Plancher and F. Cattadori (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 10—13).—The principal product of the oxidation of 2 : 4-dimethylpyrrole by means of sulphuric acid and potassium dichromate is citraconimide (methylaleinimide. T. H. P.

Synthesis of Ecgonic Acid. Richard Willstätter and Charles Hollander (*Annalen*, 1903, **326**, 79—90).—*r*-Ecgonic acid (1-methylpyrrolidone-2-acetic acid) can be synthesised from β-bromoadipic acid (prepared by addition of hydrogen bromide to Δ^β-hydromuconic acid)

by heating it with methylamine in benzene solution (compare Abstr., 1901, i, 561). A complete crystallographic comparison of the synthetical acid with the acid obtained from tropine has been made. The crystals of the characteristic copper salt have also been measured. The *methyl ester* is an oil which is completely miscible with water and boils at 165—170° under 19 mm., and at 159° under 13 mm. pressure; the boiling point (275° under 13·5 mm.) given by Willstätter and Bode (Abstr., 1901, i, 291) is erroneous. K. J. P. O.

Synthesis of Hygric and of 2-Pyrrolidinecarboxylic Acids. RICHARD WILLSTÄTTER and FRIEDRICH ETTLINGER (*Annalen*, 1903, **326**, 91—128).—The main reactions in the synthesis of hygric acid (1-methylpyrrolidine-2-carboxylic acid) from ethyl αδ-dibromopropylmalonate and methylamine have been previously described (Abstr., 1900, i, 405). When excess of methylamine was used, the pyrrolidinecarboxylic acid formed only a small portion of the products of the reaction; it was thought that the other substances produced were six-membered ring compounds, namely, the methylamide,

$$CH_2<\begin{matrix}NMe{-}CO\\CH_2{\cdot}CH_2\end{matrix}>C<\begin{matrix}NHMe\\CO{\cdot}NHMe\end{matrix},$$

which, on hydrolysis with baryta, lost 1 mol. of methylamine yielding the corresponding acid. Further investigation (compare Abstr., 1902, i, 233) showed that this methylamide was converted by treatment with hydrochloric acid into hygric acid with elimination of 2 mols. of methylamine. The methylamide is, therefore, a pyrrolidine derivative, $\begin{matrix}CH_2{\cdot}NMe\\|\\CH_2{-}CH_2\end{matrix}>C(CO{\cdot}NHMe)_2$, which, on treatment with baryta, yields the acid, 1-methylpyrrolidine-2-carboxymethylamido-2-dicarboxylic acid, $\begin{matrix}CH_2{\cdot}NMe\\|\\CH_2{-}CH_2\end{matrix}>C<\begin{matrix}CO_2H\\CO{\cdot}NHMe\end{matrix}$; the latter is converted into hygric methyl amide on heating or on boiling with water or dilute acids, carbon dioxide being eliminated.

Ethyl δ-bromopropylmalonate (Abstr., 1900, i, 405) boils at 153—154° under 9 mm., and at 164—166° under 16 mm. pressure; ethyl αδ-dibromomalonate (*loc. cit.*) is a sweet-smelling oil boiling at 176—177·5° under 13 mm. pressure, and is converted into ethyl αδ-dibromovalerate by heating with aqueous hydrobromic acid under pressure; the diamide of pyrrolidine-2 : 2-dicarboxylic acid (*loc. cit.*), prepared from the compound last mentioned by the action of ammonia, crystallises in prisms of cubical aspect belonging to the rhombic system ($a : b = 0·8461 : 1$) and melting at 162—162·5°; the *platinichloride* forms easily soluble, microscopic tetrahedra, and the *aurichloride*, rhombic plates melting at 180·5°; the *picrate*, which is very insoluble, crystallises in yellow, four- or eight-sided prisms terminating in pyramids, melting and decomposing at 234—235°. On hydrolysis, the diamide yields 2-pyrrolidinecarboxylic acid (m. p. 203—203·5°; compare Fischer, Abstr., 1901, i, 191), which gives a characteristic copper salt and forms a hygroscopic *hydrochloride* melting at 158—159°; the *aurichloride* forms leaflets melting at 160—162°; the ethyl ester, which has been previously described (*loc. cit.*), gradually changes on keeping into a solid which crystallises in needles melting at 185–186°.

The dimethylamide of 1-methylpyrrolidine-2 : 2-dicarboxylic acid, previously thought to be a six-membered ring compound (Abstr., 1900, i, 405), crystallises in rectangular plates or four-sided, monoclinic prisms [$a:b:c = 1·1127:1:1·156$; β 114°33′] melting at 122·5—123°, and is volatile without decomposition; the *aurichloride* forms small, pale yellow, right-angled prisms melting at 181°. On cautious hydrolysis with alkalis, the monomethylamide of 1-methylpyrrolidine-2 : 2-dicarboxylic acid, previously described as a methylaminomethylpiperidone (*loc. cit.*), is formed; it crystallises from water in large plates or short, rhombic prisms melting and decomposing at 137°, and is neutral in reaction; it forms a characteristic *copper* salt crystallising in blue-violet, right-angled plates with $3\frac{1}{2}H_2O$ and decomposing at 120°. Its *ethyl* ester, $\begin{matrix} CH_2\cdot NMe \\ | \\ CH_2-CH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CO_2Et \\ CO\cdot NHMe \end{matrix}$, is prepared by heating ethyl 1-methylpyrrolidine-2 : 2-dicarboxylate with methylamine in benzene solution at 150° under pressure, hygric acid, its methylamide, and the dimethylamide of 1-methylpyrrolidine-2 : 2′-dicarboxylic acid being formed at the same time; it crystallises in six-sided prisms melting at 199·5—200° and distils without decomposition.

Ethyl 1-*methylpyrrolidine*-2 : 2-*dicarboxylate*, $\begin{matrix} CH_2\cdot NMe \\ | \\ CH_2-CH_2 \end{matrix}\!\!>\!C(CO_2Et)_2$, can be prepared from the dimethylamide by prolonged boiling with alcoholic hydrochloric acid, and more readily by treating ethyl $\alpha\delta$-dibromopropylmalonate with methylamine in benzene solution at the ordinary temperature; it forms a colourless oil boiling at 130·5—131·5° under 13 mm. pressure (compare *loc. cit.*), and yields a *picrate* crystallising in four-sided plates melting at 86—87°.

The *methylamide* of 1-methylpyrrolidine-2-carboxylic acid (hygric methylamide), $\begin{matrix} CH_2\cdot NMe \\ | \\ CH_2-CH_2 \end{matrix}\!\!>\!C\cdot CO\cdot NHMe$, is formed when the monomethylamide of 1-methylpyrrolidine-2 : 2-dicarboxylic acid is boiled in aqueous solution or with dilute acids, and is always present in varying quantities in the product of the reaction of methylamine on ethyl $\alpha\delta$-dibromopropylmalonate; it is very difficult to isolate, owing to its great solubility in water, but can easily be obtained in the form of the picrate, from which it can be obtained as slender, hygroscopic needles melting at 44—46°; the *picrate* crystallises in insoluble, flattened prisms or plates melting and decomposing at 214—216°; the *aurichloride* crystallises in dark yellow plates melting at 149—150°; the *platinichloride* crystallises in orange-red crystals melting and decomposing at 197—198°.

Hygric acid (1-methylpyrrolidine-2-carboxylic acid, *loc. cit.*) can be prepared by hydrolysing the dimethylamide of 1-methylpyrrolidine-2 : 2-dicarboxylic acid with concentrated hydrochloric acid under pressure at 125°, or by heating ethyl 1-methylpyrrolidine-2 : 2-dicarboxylate with water under pressure at 160°; in addition to the derivatives already prepared by Liebermann (Abstr., 1895, i, 310) from the hygric acid, obtained by oxidising hygrine, the *aurichloride* is described, crystallising in lustrous prisms melting and decomposing at 190—195°; the *ethyl* ester is an oil with a strong alkaline reaction

boiling at 75—76° under 12 mm. pressure; the *aurichloride* of the ester crystallises in small prisms melting at 110·5°. The *methiodide*, $\begin{matrix}CH_2\cdot NMe_2I \\ | \\ CH_2\text{---}CH_2\end{matrix}\!\!>\!CH\cdot CO_2Et$, prepared from the ester, crystallises in colourless prisms softening at 82° and melting at 88—89°. The *methiodide* of ethyl 1-methylpyrrolidine-2 : 2-dicarboxylate,

$$\begin{matrix}CH_2\cdot NMe(MeI) \\ | \\ CH_2\text{------}CH_2\end{matrix}\!\!>\!C(CO_2Et)_2,$$

is not prepared so easily as that of ethyl hygrate; it forms leaflets softening at 90° and melting at 98°. Both these methiodides are hydrolysed by boiling with sodium hydroxide, giving the *sodium* salt of the methiodide of hygric acid, $\begin{matrix}CH_2\cdot NMe(MeI) \\ | \\ CH_2\text{------}CH_2\end{matrix}\!\!>\!CH\cdot CO_2Na$, which crystallises in needles softening at 205° and melting at 213—214°.

K. J. P. O.

Method of Preparation of Betaines. HANS MEYER (*Ber.*, 1903, **36**, 616—618. Compare Abstr., 1901, i, 190).—Pyridinecarboxylic acids react with alkyl iodides in the presence of aqueous sodium carbonate, giving nearly quantitative yields of betaines; under these conditions, 2 : 6-disubstituted pyridinecarboxylic acids are not changed. When the dry potassium or silver salts of such acids are subjected to prolonged treatment with methyl iodide, they are converted into the methyl esters. Betaines are thus obtained from picolinic, nicotinic, *iso*nicotinic, cinchoninic, quinolinic, and cinchomeronic acids. Pyridine-3-sulphonic acid also yields a betaine. The dicarboxylic acids, lutidinedicarboxylic, collidinedicarboxylic, and dipicolinic acids, are not converted into betaines.

The pyridinecarboxylic acid obtained by Ramsay from lutidine was held by Weidel and Herzig (*Monatsh.*, 1880, **1**, 4; Abstr., 1886, 477), to be impure *iso*cinchomeronic acid, and by Epstein (Abstr., 1885, 815) to be dipicolinic acid (2 : 6-pyridinedicarboxylic acid). As this acid yields a methyl ester when treated with methyl iodide, and not a betaine, it must be dipicolinic acid—a view completely confirmed by a comparison of the acid chlorides, diamide, and methyl ester.

K. J. P. O.

Occurrence of α-Picoline in Brown-Coal-Tar. HANS FRESE (*Zeit. angew. Chem.*, 1903, **16**, 11—12).—The bases are extracted from brown-coal-tar by means of ten per cent. sulphuric acid; the solution is then distilled in steam until it is odourless. After making alkaline with sodium hydroxide, the bases are distilled in steam; about 14 kilos. of anhydrous bases are obtained from 1000 zentners (cwts.) of tar. From the fraction boiling at 128—134°, which amounts to 150 grams, α-picoline can be prepared. The mercurichloride melts at 154°, but the platinichloride was found to melt at 183°, whilst in the literature melting points ranging from 178° to 217° are recorded. K. J. P. O.

Oximes of Quinoline- and *iso*Quinoline-bromoacetophenone. H. Ihlder (*Arch. Pharm.*, 1902, 240, 691—707. Compare also van Ark, *Inaug-Diss.*, Marburg, 1896; Scheda, *Inaug-Diss.*, Marburg, 1899).—*Quinoline-acetophenone bromide* (*quinolinephenacyl bromide*), $C_9H_7NBr\cdot CH_2\cdot CPhO,H_2O$, obtained by allowing equivalent amounts of quinoline and bromoacetophenone to remain together in ethereal solution, melts at 117—118°, or at 169° when anhydrous (the *chloride*, *aurichloride*, and *platinichloride* melt at 193—197°, 157°, and 240° respectively—van Ark). The *oxime*, $C_9H_7NBr\cdot CH_2\cdot CPh{:}NOH$, was obtained by allowing a solution of quinoline-acetophenone bromide to remain with hydroxylamine hydrochloride and sodium hydrogen carbonate in equivalent quantities in dilute alcohol solution; the liquid was afterwards exactly neutralised with hydrochloric acid, evaporated to dryness, and the residue extracted with hot water; the oxime crystallises from the solution; it melts at 207°. When quinolinephenacyl bromide and hydroxylamine hydrochloride are boiled together in alcoholic solution, *anhydro-quinoline-phenacyloxime hydrochloride*, $\begin{matrix} O\text{———————}N \\ | \qquad\qquad\quad \\ C_9H_7N\cdot CH_2 \end{matrix}\!\!>\!CPh,HCl$, is formed; this can be titrated with alkali; alkali sets free the base, which melts at 72° and forms salts with acids; of these, the *hydrochloride*, with $1H_2O$, *hydrobromide*, with $1H_2O$, *aurichloride*, and *platinichloride* were analysed; the last two melt at 159—163° and 247° respectively, the first two remain unmelted at 250°. Along with the anhydro-hydrochloride, some *hydrochloride* of *quinoline-phenacyloxime chloride*,

$$C_9H_7NCl\cdot CH_2\cdot CPh{:}NOH,HCl,1\tfrac{1}{2}H_2O,$$

is formed; this melts at 182°, evolves hydrogen when heated, leaving the anhydro-hydrochloride, and loses hydroxylamine when treated with phosphorus pentachloride or even with gold or platinum chloride. Phosphorus pentachloride has no action on the anhydro-hydrochloride.

*iso*Quinoline-acetophenone bromide (*iso*quinolinephenacyl bromide), with $\frac{1}{2}H_2O$, *chloride*, with $2H_2O$, *aurichloride*, *platinichloride*, and *mercurichloride* melt at 202°, 185—189°, 140—145°, 232—239°, and 240—241° respectively—Scheda. The oxime of the bromide melts at 195—205°. *Anhydro*iso*quinolinephenacyl oxime hydrochloride* and *platinichloride* do not melt at 250°; the *aurichloride* melts at 167—169°, the base itself at 121°; half the chlorine in the hydrochloride can be titrated with an alkali. Along with the hydrochloride just mentioned, some iso*quinolinephenacyloxime chloride*, $C_9H_7NCl\cdot CH_2\cdot CPh{:}NOH,1\frac{1}{2}H_2O$, is formed; this melts at 147° and is neutral in reaction; when heated at 100°, it is transformed into the anhydro-hydrochloride, and gold and platinum chlorides eliminate hydroxylamine from it. Phosphorus pentachloride has no action on the anhydro-chloride; with the oxime chloride, it yields a substance which, judging from the analysis of its aurichloride (this does not melt at 250°), may be dichloro*iso*quinolinechloroacetanilide, $C_9H_7NCl\cdot CH_2\cdot CCl_2\cdot NHPh$.

When pyridineacetonyl chloride, $C_5H_5NCl\cdot CH_2\cdot CMeO$, is boiled with an equivalent amount of hydroxylamine hydrochloride in aqueous

solution, pyridineacetonyloxime chloride, $C_5H_5NCl\cdot CH_2\cdot CMe\colon NOH$, is formed (Knuttel, Abstr., 1899, 229). C. F. B.

Benzylquinoline Chloride and *d*-Camphorsulphonate. ALBERT REYCHLER (*Bull. Soc. chim.*, 1903, 29, [iii], 134—137).—Benzylquinoline chloride was prepared by heating together at 100° molecular quantities of benzyl chloride and quinoline mixed with water and alcohol in a vessel communicating with the air by a narrow tube. The product, recrystallised from alcohol, acquires a pink tint at 130—140°, melts and decomposes at about 170°, and contains about 1·3 per cent. of water of crystallisation (compare Claus and Himmelmann, Abstr., 1881, 182).

Benzylquinoline d-*camphorsulphonate*, prepared by the addition of silver *d*-camphorsulphonate to the foregoing salt dissolved in alcohol, crystallises in brilliant laminæ, melts at 122°, and is readily soluble in water or alcohol, slightly so in ether or benzene; it contains in this form 3·3 to 4·2 per cent. of water, and, when anhydrous, becomes coloured at 130—140° and melts to a reddish liquid at 150—156°. Fractional crystallisation of the hydrated salt from a mixture of ethyl acetate and acetone did not effect any separation into isomerides, the fractions having $[\alpha]_D$ +11·20 to +11·56 in water and +24·33 in alcohol, which would give $[\alpha]_D$ +23·2 and +49·1 respectively for free camphorsulphonic acid in these solvents, the values found being somewhat lower, namely, +21·5 and +43·5, whence it is concluded that the nitrogen atom in this salt is inactive (compare this vol., i, 23). T. A. H.

3 : 7-Dimethylacridine. O. HAASE (*Ber.*, 1903, 36, 588—590).—2 : 8-*Diamino*-3 : 7-*dimethylacridine*,

$$\begin{array}{l}\quad\;\; CMe\colon CH\cdot C\cdot CH\cdot CH\cdot CH\colon CMe \\ NH_2\cdot C{=\!=\!=}CH\;\; C\cdot N{-}CH\cdot CH\colon C\cdot NH_2\end{array},$$

prepared by heating tetra-aminoditolylmethane with dilute hydrochloric acid, crystallises from dilute alcohol in yellow tablets and melts above 300°; the hydrochloride forms orange-yellow needles. 3 : 7-*Dimethylacridine*, $C_6H_3Me<\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}>C_6H_3Me$, prepared by treating the preceding compound with nitrous acid, crystallises from dilute alcohol, forms colourless needles, and melts at 176°. T. M. L.

7-Phenylhydro-β-naphthacridine and its Nitro-derivatives. O. HAASE (*Ber.*, 1903, 36, 591—594).—7-*Phenylhydro-β-naphthacridine*, $C_{10}H_6<\begin{smallmatrix}CHPh\\ NH\end{smallmatrix}>C_{10}H_6$, prepared by boiling an alcoholic solution of β-naphthylamine and benzylidene-β-naphthylamine, or by heating in an autoclave a mixture of β-naphthylamine, its hydrochloride and benzaldehyde, crystallises from alcohol in colourless needles and melts at 230°; it separates from pyridine in yellow flakes containing pyridine of crystallisation and melting at 200°; it has no basic properties and is very readily oxidised to the corresponding acridine.

7-p-*Nitrophenylhydro-β-naphthacridine*, $NH<\begin{smallmatrix}C_{10}H_6\\ C_{10}H_6\end{smallmatrix}>CH\cdot C_6H_4\cdot NO_2$,

prepared by a similar method, crystallises from acetic acid in yellowish-red needles and melts at 291°. The m-*nitro*-compound crystallises from acetic acid in red prisms and melts at 270°. It is prepared from m-*nitrobenzylidenenaphthylamine*, a compound which crystallises from alcohol in yellow tablets and melts at 90°. o-*Nitrobenzylidene-naphthylamine* crystallises from alcohol in yellow flakes, melts at 91°, and could not be converted into a hydronaphthacridine. T. M. L.

Decomposition of Phenylhydrazones. OTTO ANSELMINO (*Ber.*, 1903, **36**, 580—582).—Salicylaldehydephenylhydrazone, when heated at 294°, suddenly decomposes, the temperature rises to 380—390°, and the products formed distil; they consist of benzene, ammonia, *o*-cyanophenol (as ammonium salt), and aniline. Some of the aniline combines with *o*-cyanophenol to form *aniline-o-cyanophenoxide*,

$$CN\cdot C_6H_4\cdot O\cdot NH_3Ph,$$

which crystallises from water in long, flat needles and melts at 78°. W. A. D.

Reduction of Ketohydrazines. Benzhydrylhydrazine. AUGUST DARAPSKY (*J. pr. Chem.*, 1903, [ii], **67**, 112—136).—*Benzhydrylhydrazine*, $CHPh_2\cdot NH\cdot NH_2$, prepared by reduction of diphenylmethylene hydrazine with sodium amalgam in alcoholic solution in the cold and isolated by means of its nitrate, is a white, crystalline solid melting at 58—59° and distilling at 188° under 12 mm. pressure; it forms a thick, colourless oil, which, on exposure to the air, solidifies and rapidly becomes yellow. The *nitrate*, which is sparingly soluble in cold water, melts and decomposes at 182—183°, the *hydrochloride* at 209°, the *picrate* at 160°, the *oxalate* at 169°, and the *nitrite* at 84°; all form well-characterised, crystalline compounds.

Although benzhydrylhydrazine distils unchanged under reduced pressure, it decomposes when heated at the ordinary pressure, forming tetraphenylethane and diphenylmethane. When heated with dilute hydrochloric acid, it breaks up almost quantitatively into α-chlorodiphenylmethane and hydrazine chloride. Tetraphenylethane is also formed on oxidation with mercuric oxide in benzene solution.

Nitrosobenzhydrylhydrazine, $CHPh_2\cdot N(NO)\cdot NH_2$, obtained by acting on the chloride with sodium nitrite and acetic acid at low temperatures, melts at 92°. E. F. A.

Reduction of Ketohydrazines. Benzhydrylhydrazine and *sym.*-Dibenzhydrylhydrazine. AUGUST DARAPSKY (*J. pr. Chem.*, 1903, [ii], **67**, 164—192. Compare preceding abstract).—*Benzylidene-nitrosobenzhydrylhydrazine*, $CHPh_2\cdot N(NO)\cdot N{:}CHPh$, formed by the action of benzaldehyde on nitrosobenzhydrylhydrazine, or of nitrous acid on benzylidenebenzhydrylhydrazone, crystallises in slender, yellow needles and melts and decomposes at 96°. o-*Hydroxybenzylidenenitroso-benzhydrylhydrazine*, formed by the action of salicylaldehyde on nitrosobenzhydrylhydrazine, crystallises in slender, yellow, glistening needles and melts and decomposes at 100°.

Attempts to prepare benzhydrylazoimide by heating nitrosobenzhydrylhydrazine with dilute sulphuric acid resulted in the formation of benzhydrol, benzhydrylamine, and azoimide of benzhydrol ether,

and of a thick, colourless *oil*, which boiled at 185° under 40 mm. pressure, gradually solidified, and melted at 45°, contained about half the nitrogen required for benzhydrylazoimide, and evolved azoimide when boiled with dilute sulphuric acid. When heated with phosphoric acid or acetic acid, nitrosobenzhydrylhydrazine yields benzhydrol and benzhydrylamine. The action of sodium nitrite on benzhydrylhydrazine hydrochloride in presence of excess of sulphuric acid leads to the formation of nitrosobenzhydrylhydrazine and of a slowly solidifying *oil*, which boils at 170° under 16 mm. pressure, and contains about half the amount of nitrogen required for benzhydrylhydrazine.

Diacetylbenzhydrylhydrazine, $CHPh_2\cdot N_2HAc_2$, formed by the action of acetic anhydride on benzhydrylhydrazine, crystallises in thick, glistening plates, melts at 197—198°, and is easily soluble in chloroform, warm benzene, or alcohol.

Dibenzoylbenzhydrylhydrazine crystallises in leaflets, melts at 262°, and is easily soluble in warm acetic acid, but only slightly so in other solvents.

Benzhydrylsemicarbazide, $CHPh_2\cdot NH\cdot NH\cdot CO\cdot NH_2$, formed by the action of potassium cyanate on benzhydrylhydrazine hydrochloride in aqueous solution, crystallises in colourless leaflets, sinters at 150°, is completely melted at 160°, and is easily soluble in alcohol, acetic acid, or chloroform, but less so in water or benzene.

Benzhydryl-4-phenylthiosemicarbazide, $CHPh_2\cdot NH\cdot NH\cdot CS\cdot NHPh$, formed by mixing benzhydrylhydrazine and phenylthiocarbimide in alcoholic solution, crystallises in clusters of white prisms, melts at 163—164°, and is easily soluble in benzene, chloroform, or warm alcohol.

With acetylacetone, benzhydrylhydrazine condenses to form 1-*benzhydryl*-3 : 5 *dimethylpyrazole*, which crystallises in white, matted needles, melts at 108—109°, and is easily soluble in alcohol, ether, chloroform, benzene, or boiling light petroleum, and possesses basic properties, being soluble in dilute hydrochloric acid. It does not give Knorr's pyrazoline reaction.

When warmed with ethyl acetoacetate, benzhydrylhydrazine forms 1-*benzhydryl*-3-*methyl*-5-*pyrazolone*, which crystallises in colourless, glistening prisms, begins to sinter at 190°, is completely melted at 195°, and is easily soluble in glacial acetic acid or warm chloroform or benzene ; it is easily soluble in alkalis, less easily so in dilute acids. 4-iso*Nitroso*-1-*benzhydryl*-3-*methyl*-5-*pyrazolone*, formed by the action of nitrous acid on benzhydrylmethylpyrazolone, crystallises from alcohol in glistening, yellow needles, which contain C_2H_6O and melt and decompose at 182°.

1-*Benzhydryl*-4-*benzylidene*-3-*methylpyrazolone*, formed by heating the pyrazolone with benzaldehyde at 150°, crystallises from alcohol in slender, yellowish-red needles, melts at 176°, and is soluble in benzene and chloroform. 1-*Benzhydryl*-4-p-*tolylhydrazone*-3-*methylpyrazolone*, formed by the action of toluenediazonium sulphate on benzhydrylmethylpyrazolone in alkaline solution, crystallises in long, yellowish-red needles, melts at 162—163° to a scarlet-red liquid, and is easily soluble in ether, chloroform, or benzene.

Benzylidenebenzhydrylhydrazone is formed when benzhydrylhydrazine

hydrochloride is shaken with benzaldehyde in aqueous solution. It crystallises from alcohol in glistening, colourless needles, melts and decomposes at 85°, is easily soluble in ether, chloroform, benzene, glacial acetic acid, or warm alcohol, and, when exposed to the air, gradually decomposes into a yellow mass, which smells of benzaldehyde.

Benzophenonebenzhydrylhydrazone is formed when benzhydrylhydrazine is heated with benzophenone at 150°. It crystallises in colourless prisms, melts at 91°, yields, with acetic anhydride, an *acetyl* derivative, $CHPh_2 \cdot NAc \cdot N{:}CPh_2$, which crystallises in small, thick, glistening plates and melts at 145°, and with sodium nitrite in glacial acetic acid solution it forms a *nitroso*-derivative,

$$CHPh_2 \cdot N(NO) \cdot N{:}CPh_2,$$

which crystallises in light yellow needles and melts and decomposes at 80—81°.

Reduction of benzophenonebenzhydrylhydrazine with sodium amalgam leads to the formation of s-*dibenzhydrylhydrazine*,

$$CHPh_2 \cdot NH \cdot NH \cdot CHPh_2,$$

which is also formed along with benzhydrylamine by reduction of diphenylketazine with sodium amalgam; it crystallises in long, colourless, glistening needles, commences to sinter at 120°, is completely melted at 133°, and is easily soluble in glacial acetic acid or warm alcohol.

Dibenzhydrylhydrazine is converted into tetraphenylethane when heated at 150—160°, when heated with mercuric oxide in alcohol or benzene, or when treated with amyl nitrite in hot glacial acetic acid solution.

Dibenzhydrylhydrazine hydrochloride crystallises in small, glistening leaflets, melts and decomposes at 205°, and is insoluble in water or ether, but easily soluble in alcohol. When boiled with excess of dilute hydrochloric acid, dibenzhydrylhydrazine yields α-chlorodiphenylmethane and hydrazine hydrochloride, but more slowly than does monobenzhydrylhydrazine.

Nitrosodibenzhydrylhydrazine, $CHPh_2 \cdot N(NO) \cdot NH \cdot CHPh_2$, formed by the action of sodium nitrite on dibenzhydrylhydrazine in glacial acetic acid solution or by the action of amyl nitrite in the cold, crystallises in slender, white needles, sinters and melts and decomposes at 135°, and closely resembles dibenzhydrylhydrazine in its solubilities, but is only sparingly soluble in cold glacial acetic acid.

Acetyldibenzhydrylhydrazine crystallises in white needles, melts at 158°, and is easily soluble in benzene, chloroform, or hot alcohol. *Benzoyldibenzhydrylhydrazine*, formed by the action of benzoyl chloride on dibenzhydrylhydrazine in benzene solution in presence of sodium carbonate, crystallises in thick, colourless prisms, sinters at 150°, and melts at 155°. When heated with benzoyl chloride, dibenzhydrylhydrazine is converted into dibenzoylbenzhydrylhydrazine, which melts at 262°.

When reduced with zinc dust and glacial acetic acid in alcoholic solution, diphenylketazine yields benzhydrylamine and benzpinacone, the latter resulting from an intermediate formation of benzhydrylamine.

G. Y.

Preparation of 1-Phenyl-5-methyl-3-pyrazolone and its Derivatives. KARL MAYER (*Ber.*, 1903, 36, 717—718).—1-Phenyl-5-methyl-3-pyrazolone, $NPh<\begin{matrix}CMe{:}CH\\ NH-CO\end{matrix}$, can be prepared in good yield by the action of phosphorus trichloride on a mixture of benzoyl- or acetylphenylhydrazine and ethyl acetoacetate. It is converted by heating with phosphorus oxychloride into the corresponding 5-chloropyrazole, $NPh<\begin{matrix}N{=}CMe\\ CCl{:}CH\end{matrix}$, which yields a methiodide and methochloride, from which *iso*antipyrine and *iso*thioantipyrine can be prepared. T. M. L.

New Synthesis of *o*-Diazine [Pyridazine]. R. MARQUIS (*Compt. rend.*, 1903, 136, 368—370. Compare Abstr., 1902, i, 483).—The acetin of nitrosuccinaldehyde, $CHO{\cdot}CH(NO_2){\cdot}CH{:}CH{\cdot}OAc$, is converted by hydrazine in methyl alcoholic solution into pyridazine, $CH\leqslant\begin{matrix}CH{=}N\\ CH{\cdot}CH\end{matrix}\geqslant N$; in all probability, maleic aldehyde or fumaraldehyde is formed as an intermediate product. Pyridazine, which was prepared by Täuber (Abstr., 1895, i, 301), melts at $-8°$, boils at 205° (corr.) under 755·5 mm. pressure, has a sp. gr. 1·1108 at 15°, and forms an aurichloride melting at 170° (Täuber; 110°). The *picrate* melts and decomposes at 169°; the *platinichloride*, $(C_4N_2H_4)_2PtCl_4$, forms pale yellow, insoluble crystals, whilst the *platinichloride*, $(C_4N_2H_4)_2,H_2PtCl_6$, crystallises in soluble, orange-yellow prisms. Attempts to reduce the pyridazine by sodium and alcohol to an isomeride of piperazine were unsuccessful; it was mainly decomposed with the formation of ammonia and a small quantity of tetramethylenediamine.

K. J. P. O.

Action of Mercurous Nitrate and of Neutral Mercurosomercuric Reagent on Antipyrine. A. MOULIN (*Bull. Soc. chim.*, 1903, [iii], 29, 201—203).—When solutions of antipyrine and of mercurous nitrate, each dissolved in saturated aqueous solutions of potassium nitrate, are mixed, there is precipitated the *compound* $C_{11}H_{12}ON_2,Hg(NO_3)_2$, which separates from warm alcohol in small, white crystals, is soluble in alcohol, dilute nitric acid, and solution of sodium hydroxide, slightly so in water. The neutral mercurosomercuric reagent is prepared by dissolving mercury (5 grams) in 50 c.c. of nitric acid diluted with a like quantity of water; a current of air is then aspirated through the solution to remove nitrogen oxides, the liquid diluted with 400 c.c. of a saturated aqueous solution of potassium nitrate, and neutralised by the addition of excess of yellow mercuric oxide. This reagent, when added to solutions of antipyrine, gives, in addition to the product, $C_{11}H_{12}ON_2,Hg(NO_3)_2$, already described, a precipitate consisting of the *compound* $C_{11}H_{12}ON_2,Hg_2(NO_2)_2$, a brilliant red powder insoluble in water, but slightly so in nitric acid, and the *substance* $C_{11}H_{12}ON_2,Hg(NO_2)_2$, a yellowish-brown, crystalline powder, slightly soluble in water and readily so in nitric acid. Both these compounds explode when heated to 205—210°, producing a voluminous charred residue and gaseous products having an alliaceous odour. T. A. H.

[Phenyldiethyltriazine.] EUGEN BAMBERGER and MICH. TICHVINSKY (*Ber.*, 1903, 36, 662—663).—A reply to C. Harries (compare this vol., i, 293). Purely polemical. J. J. S.

Action of Alkalis and Alcohols on *ortho*-Chloronitrobenzene. K. BRAND (*J. pr. Chem.*, 1903, [ii], 67, 145—163).—When reduced with a large excess of a concentrated solution of sodium methoxide, *o*-chloronitrobenzene yields *o*-chloroazobenzene. If the excess of sodium methoxide is slight, the product is *o*-dichloroazoxybenzene, but if the solution of sodium methoxide is dilute, *o*-azoxyanisole (Starke, Abstr., 1899, i, 589) is obtained.

o-*Dichloroazobenzene* crystallises in red needles, melts at 136°, and is easily soluble in hot alcohol. o-*Dichloroazoxybenzene* crystallises in delicate, light-yellow needles, melts at 56°, and is easily soluble in cold alcohol. Reduction of *o*-chloronitrobenzene with sodium ethoxide results chiefly in the formation of *o*-chloroaniline, along with a small quantity of *o*-dichloroazobenzene if the solution is concentrated, *o*-dichloroazoxybenzene if the solution is dilute.

By reducing *o*-chloronitrobenzene with aqueous methyl-alcoholic potassium hydroxide, *o*-nitroanisole, with aqueous ethyl-alcoholic potassium hydroxide, *o*-nitrophenetole, is obtained.

Electrolytic reduction by Boehringer's method (Chilesotti, Abstr., 1901, i, 587) of *o*-dichloroazo- and azoxy-benzenes leads to the formation of *o*-chloroaniline and o-*dichlorobenzidine*, which forms greyish-white, small crystals, melts at 133°, and, when diazotised and coupled with "R" salt, yields a red dye.

o-Azoxyanisole, which can be formed by the action of sodium methoxide on *o*-nitrophenetole (compare Gattermann and Ritschke, Abstr., 1890, 1119), is electrolytically reduced to *o*-anisidine and *o*-dianisidine.

o-Nitroanisole is electrolytically reduced, in presence of sodium acetate, to *o*-azoxyanisole, in presence of stannous chloride or copper powder and hydrochloric acid to chloro-*o*-anisidine, and in presence of copper and sulphuric acid to *o*-anisidine. G. Y.

Formation of Azo-compounds. Reduction of *o*-Nitrobenzyl Alcohol. PAUL FREUNDLER (*Compt. rend.*, 1903, 136, 370—373).—Although, on reducing by sodium hydroxide and zinc dust in the presence of alcohol a mixture of nitrobenzene and the acetal of *p*-nitrobenzaldehyde, benzeneazo-*p*-benzaldehyde is formed, the reduction of a mixture of nitrobenzene and *o*-nitrobenzyl alcohol yields only azobenzene. When *o*-nitrobenzyl alcohol is reduced under the same conditions, a mixture of eight substances is obtained. 1. *o*-Aminobenzaldehyde is formed in very small quantity. 2. *o*-Aminobenzyl alcohol. 3. *Bisanhydroaminobenzaldehyde*, $C_6H_4<\substack{CH:N \\ N:CH}>C_6H_4$, crystallises in white needles melting at 84°, boiling at 212—216° under 19 mm. pressure, and is insoluble in dilute acids and water, but soluble in concentrated hydrochloric acid with a yellow coloration; the *platinichloride* is decomposed by water; no benzoyl derivative could be obtained. 4. A compound identical with that obtained by Friedländer (Abstr., 1884, 1019) by the action

of dilute hydrochloric acid on *o*-aminobenzaldehyde; it is a yellow resin of basic properties, soluble in concentrated hydrochloric acid, does not form a hydrazone, and reduces ammoniacal silver oxide slowly when heated; it is probably represented by the formula

$$C_6H_4<\begin{matrix}CH(OH)\cdot NH\\ N\!=\!=\!=\!=\!=\!CH\end{matrix}>C_6H_4,$$

and not the formula $CHO\cdot C_6H_4\cdot N\!:\!CH\cdot C_6H_4\cdot NH_2$, suggested by Friedländer, as when distilled under a pressure of 17 mm. the bisanhydroaminobenzaldehyde, mentioned above, is formed with elimination of water, and distils at 250°. 5. *Indazyl-o-benzoic acid,*

$$C_6H_4<\begin{matrix}CH\\ N\end{matrix}>N\cdot C_6H_4\cdot CO_2H,$$

crystallises in plates melting at 203—204°, on oxidation with chromic acid yields *o*-azobenzoic acid, and resembles very closely indazyl-*m*-benzoic acid (Abstr., 1893, i, 210). 6. A very small quantity of the *acid*, $OH\cdot CH_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CO_2H$, which formed red crystals melting at 195°. 7. Anthranilic acid. 8. The *amide*, $(C_{14}H_8O_2N_2)_4$, is a yellow, neutral substance, which sublimes and melts at 294°; it is converted by alcoholic sodium hydroxide into an amino-acid. K. J. P. O.

Decomposition of Diazonium Salts with Phenols. JAMES F. NORRIS, B. G. MACINTIRE, and W. M. CORSE (*Amer. Chem. J.*, 1903, **29**, 120—129).—It has been shown by Hirsch (*J. pr. Chem.*, 1885, [ii], **32**, 117) that in the preparation of phenol from aniline by means of the diazo-reaction *p*-dihydroxydiphenyl is formed.

If a phenol is mixed with a small quantity of water at 90° and treated cautiously with a solution of a benzenediazonium salt, a vigorous reaction occurs and a dark, heavy oil separates. When phenol is used, the product consists of *p*-hydroxydiphenyl, *o*-hydroxydiphenyl, phenyl ether, and tarry substances. The yield of *p*-hydroxydiphenyl from 40 grams of aniline was 20 grams, and that of the *o*-compound 1·5 grams. The diphenyl compounds are best separated from the mixture by distillation with superheated steam.

In the case of catechol, the chief products are dihydroxydiphenyl, *o*-hydroxydiphenyl ether, and an oil; this oil yields a small quantity of a crystalline substance which melts at 147·5—148·5° and is probably an isomeride of the dihydroxydiphenyl.

o-*Hydroxydiphenyl ether* crystallises from hot water in long needles, melts at 105—106°, has an aromatic odour, and is readily soluble in carbon disulphide, benzene, or glacial acetic acid; the yield from 40 grams of aniline amounted to 4·6 grams. The *acetyl* derivative is a thick oil which boils at 358—360° (uncorr.). The *methyl* ether forms long, flat, six-sided crystals and melts at 77°.

Dihydroxydiphenyl melts at 136—136·5°, boils above 360°, and is very soluble in alcohol, chloroform, or ether, and less so in carbon disulphide, light petroleum, or hot water; its solubility in cold water is 1·6 grams per litre. It gives a light green coloration with ferric chloride, which is changed to a deep violet on addition of sodium carbonate. The yield of this substance from 40 grams of aniline amounted to 9 grams. The *diacetyl* derivative forms long, six-sided

crystals and melts at 77—77·5°. The compound is probably 3 : 4-dihydroxydiphenyl.

When resorcinol was treated with a benzenediazonium salt, no diphenyl derivatives could be isolated. In the case of quinol, the reaction proceeds in a manner analogous to that of catechol; the chief product, however, is *p*-hydroxyphenyl ether. E. G.

Preparation of Mixed Aminoazo-compounds. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 131860).—The condensation products from primary aromatic amines, formaldehyde, and sulphurous acid or the hydrogen sulphites have the general formula $R \cdot NH \cdot CH_2 \cdot SO_3H$. They readily allow the entry of the diazo-group in the *o*- or *p*-position, and the $\cdot CH_2 \cdot SO_3H$ group may then be eliminated by warming with alkalis, alkali carbonates, or mineral acids.

Thus the sodium salt of methylaniline-ω-sulphonic acid with *p*-nitrobenzenediazonium chloride yields *p*-nitrobenzeneazoaniline,

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH_2,$$

melting at 210—212° (Noelting and Binder, *Ber.*, 1887, **20**, 3015, give 203—205°). p-*Nitrobenzeneazo*-o-*toluidine* melts at 200—201°.

The corresponding compound from methyl-*o*-toluidine-ω-sulphonic acid and β-naphthalenediazonium chloride melts at 175°.

The mixed *tetrazo*-compound, $C_{12}H_8(N_2 \cdot C_6H_4 \cdot NH_2)_2$, from methylaniline-ω-sulphonic acid and methyl-*o*-toluidine-ω-sulphonic acid with diazotised benzidine, melts at 160°.

These colouring matters closely resemble aminoazobenzene in their properties. C. H. D.

The Albumin Reaction of Acids. Franz Mylius (*Ber.*, 1903, **36**, 775—778).—Egg albumin is not precipitated by orthophosphoric, orthotelluric, boric, oxalic, acetic, formic, or benzoic acid, but is readily precipitated from dilute solution by a number of complex acids, including metaphosphoric, molybdic, tungstic, phosphotungstic, *allo*telluric, and tannic acids. It is stated that the acids contained in the first group all have simple compositions in aqueous solution, whereas the acids of the second group have complex compositions in aqueous solution, in fact contain "paired" molecules.

A number of common acids precipitate egg albumin if a sufficiently strong solution of the acid is taken. The following numbers indicate the minimum concentration (in percentages) of each acid required to produce an immediate precipitate at 18°. Nitric, 2; chloric, 3; bromic, 20; iodic, 20; hydrochloric, 8; hydrobromic, 3; hydriodic, 3; hydrofluoric, 20; sulphuric, 20; selenic, 27; chromic, 0·5.

The time required for the precipitation to be complete varies with the concentration of the acid and also with the temperature.

The precipitates are regarded as unstable saline derivatives of an insoluble modification of the albumin. As a rule, this modification remains behind when the acid is removed by washing with water.

J. J. S.

Carbohydrates from the Globulins of Blood-serum. Leo Langstein (*Chem. Centr.*, 1903, i, 239; from *Münch. med. Woch.*, 49, 1876—1877. Compare Abstr., 1901, i, 108; 1902, i, 65).—By means of hydrogen bromide, certain carbohydrates can be split off from the globulins of the blood; one contains nitrogen, but it is not glucosamine; it yields a crystalline benzoyl compound. Another is lævorotatory, non-fermentable, and yields a crystalline osazone. The third and most important is dextrose. W. D. H.

Mucoids. William J. Gies (*Proc. Amer. Physiol. Soc.*, 1902, xiii; *Amer. J. Physiol.*, 8).—Osseo-mucoid is a normal constituent of all bones. Connective tissue mucoid combines with other proteids; thus, an alkaline solution of potassio-mucoid and gelatin yields, with acid, a precipitate more promptly than a solution of the mucoid salt alone. Acidification of tissue extracts will not completely precipitate the mucoid. Precipitated mucoid shows no combining power with acids; in the hydration of mucoid by pepsin-acid, however, the acid combines with the dissolved proteid products formed in the process. The blood-serum of a rabbit which had been treated with several subcutaneous or intraperitoneal injections of potassio-mucoid produced precipitates in neutral and slightly acid solutions of the latter proteid substance. W. D. H.

Optical Activity of Nucleo-proteids. Arthur Gamgee and Walter Jones (*Amer. J. Physiol.*, 1903, 8, 44).—Whereas all simple proteids are lævorotatory, hæmoglobin is dextrorotatory, although its proteid globin is lævorotatory (Gamgee and Croft Hill). In the present research, six preparations of nucleo-proteid from pancreas, thymus, and suprarenal were obtained in a pure condition. They are all dextrorotatory, the specific rotation varying from $+37·5°$ to $+97·9°$. W. D. H.

Glucothionic Acid. Phoebus A. Levene (*Proc. Amer. Physiol. Soc.*, 1902, xi; *Amer. J. Physiol.*, 8).—In the preparation of nucleic acid by the picric acid-alcohol method, a carbohydrate is precipitated with the acid. In yeast, bacteria, pancreas, and liver, this resembles glycogen. In the spleen, it resembles chondroitin-sulphuric acid; it contains sulphuric acid in organic combination, and gives the barium test for glycuronic acid; it, however, contains 3 per cent. of sulphur and 5·4 per cent. of nitrogen. It also differs from chondroitin-sulphuric acid in that the purple colour given with orcinol-hydrochloric acid remains unchanged for days, and does not soon change into green. It is considered probable that the substance from the spleen is not unlike the glucosamic acid of Fischer combined with sulphuric acid. W. D. H.

Glucophosphoric Acid. Phoebus A. Levene (*Proc. Amer. Physiol. Soc.*, 1902, xi—xii; *Amer. J. Physiol.*, 8).—The phosphorus-containing substance first obtained by Palladin from seeds can be decomposed, so that 30 per cent. of its organic part can be split off as a pentose. It

yields neither glycerol nor purine bases; it contains about 15 per cent. of organic phosphorus, 1·8 per cent. of nitrogen, and 50 per cent. of ash, mainly calcium-magnesium phosphate. W. D. H.

Nucleic Acid. PHOEBUS A. LEVENE (*Proc. Amer. Physiol. Soc.*, 1902, xii; *Amer. J. Physiol.*, 8).—Attention was directed towards the presence or absence of glycerol, carbohydrate, and pyrimidine derivatives in the nucleic acid of spleen and pancreas. Glycerol was not found; carbohydrate could not be isolated, but five nucleic acids were obtained, which all gave furfuraldehyde reactions; thymin was also isolated. A substance was also obtained as a picrate which could be transformed into a hydrogen sulphate; in elementary composition, it is not unlike Kossel's cytosine, but is nearer to episarcine; it is perhaps amino-hydroxypyrimidine. W. D. H.

[Chlorophyll and Hæmoglobin.] NADINE SIEBER-SCHUMOFF (*Chem. Centr.*, 1903, i, 239; from *Münch. med. Woch.*, 49, 1874—1876).—A *résumé* of work by Nencki; hæmoglobin yields hæmatoporphyrin, $C_{16}H_{18}O_3N_2$, and mesoporphyrin, $C_{16}H_{18}O_2N_2$; chlorophyll yields phylloporphyrin, $C_{16}H_{18}ON_2$. From both mesoporphyrin and phylloporphyrin hæmopyrrole, $C_8H_{13}N$, and urobilin, $C_{32}H_{10}O_7N_4$, are obtainable.
W. D. H.

Mesoporphyrin. JEAN ZALESKI (*Bull. Acad. Sci. Cracow*, 1902, 512—532).—The hydrochloride of mesoporphyrin, prepared according to Nencki and Zaleski's method (Abstr., 1901, i, 434) by reducing hæmin by hydriodic acid and phosphonium iodide, has been obtained in better yield (40 per cent.). A number of new analyses have led to the formula $C_{17}H_{20}O_2N_2Cl$, which now lies very near to that of the hydrochloride of hæmatoporphyrin, $C_{17}H_{20}O_3N_2Cl$. Both hydrochlorides crystallise in needles, those of mesoporphyrin generally forming star-shaped groups; both belong to the rhombic system and exhibit polychroism, transmitting a dark brown colour in the direction of greatest, and a brown-yellow in that of least, length. The hydrochloride of hæmatoporphyrin is more soluble than that of mesoporphyrin.

The esters of mesoporphyrin are well characterised, whereas those of hæmatoporphyrin are amorphous. *Mesoporphyrin methyl ester*, $C_{17}H_{18}O_2N_2Me$, is prepared by heating the hydrochloride with methyl alcohol containing 5—12 per cent. of hydrogen chloride for 4—9 hours at 100°; it crystallises in star-shaped groups of needles sintering at 190° and melting at 213—214°. The corresponding *ethyl* ester, $C_{17}H_{18}O_2N_2Et$, forms thin plates with a violet, metallic lustre melting at 202—205°. Both esters have a spectrum identical with that of the hydrochloride of mesoporphyrin in alcoholic solution. They are stable towards alkali hydroxides and concentrated ammonia, but are hydrolysed by boiling acids.

It has been ascertained that treatment of hæmatoporphyrin with hydriodic acid and phosphonium iodide leads to the formation of mesoporphyrin, which has been recognised by conversion into the ethyl ester.

The hydrochloride of mesoporphyrin gives, in aqueous solution, crystalline precipitates with metallic acetates; thus, there were prepared ammonium, potassium, sodium, calcium, barium, magnesium, zinc, copper, and silver salts. The *ammonium* salt crystallises in small needles and in rhombs; the *zinc*, $(C_{17}H_{18}O_2N_2)_2Zn$, and the *copper* salt do not melt at 310°. The esters of mesoporphyrin also form salts; they all crystallise well and are soluble in organic solvents; the *copper* salt of the ethyl ester, $(C_{19}H_{22}O_2N_2)_2Cu$, melts at 211°.

Mesoporphyrin, $C_{17}H_{19}O_2N_2$, is prepared from the hydrochloride by treatment with sodium hydroxide and subsequent precipitation with acetic acid; it is soluble both in dilute alkalis and acids. Cryoscopic determinations of the mol. weight of mesoporphyrin and the ethyl ester show that they have formulæ double the empirical formulæ given above. K. J. P. O.

Presence of Small Quantities of Trypsin in Commercial Pepsins. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm. Chim.*, 1903, [vii], 17, 164—169).—The authors have studied the action of commercial pepsins on fibrin liquefied by means of hydrochloric or oxalic acid. The small amount of action observed in the solutions after neutralisation is due to trypsins, as shown by the brown colour developed in them by tyrosinase and by the fact that after preliminary treatment with acids, whereby the trypsin is destroyed, pepsins do not cause any digestion in the neutral solutions. G. D. L.

Extraction of the Active Substance of Suprarenal Capsules. JOKICHI TAKAMINE (D.R.-P. 131496).—Adrenalin (compare Abstr., 1902, ii, 217) is prepared by concentrating an aqueous extract of the suprarenal capsules and, after rendering alkaline, precipitating by the addition of an ammonium salt or by passing a current of carbon dioxide. The crystalline product may be recrystallised from hot water. C. H. D.

Adrenalin. JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, 1902, xxix—xxx; *Amer. J. Physiol.*, 8).—More than thirty analyses of adrenalin show that there is no uniformity of composition; repeated precipitation raises the amount of carbon. The extremes found are: C, 56·5 to 58·9; H, 4·7 to 7·2; N, 7·6 to 10·6 per cent. W. D. H.

Behaviour of Suprarenal Extracts to Fehling's Solution. JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, 1902, xxx—xxxi; *Amer. J. Physiol.*, 8).—Whilst extracts of the gland require prolonged boiling to effect reduction of Fehling's solution, salts of epinephrin or adrenalin reduce Fehling's solution rapidly, even below the boiling point. W. D. H.

Oxidation of Epinephrin and Adrenalin with Nitric Acid. JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, 1902, xxxi—xxxii; *Amer. J. Physiol.*, 8).—The products obtained by the oxidation of epinephrin and adrenalin are identical. Special attention is drawn to the products obtained by the use of nitric acid; these are mainly oxalic acid

and a crystalline hygroscopic salt (? oxalate) of a nitrogenous base, called the coniine-piperidine-like substance on account of its offensive and penetrating odour; this base is liberated by the addition of alkali. When fused with powdered potassium hydroxide, an odour like that of pyrrolidine is obtained, later that of amines, and finally pyrrole itself is evolved. W. D. H.

Influence of Carbon Dioxide on Diastasic Action. Otto Mohr (*Chem. News*, 1903, 87, 39—40).—In the author's experiments, emulsions of 2·5 grams of the air-dried starch in 200 c.c. of water were treated with 5 c.c. of cold extract of malt and maintained at a temperature of 53—55°, but after two hours were plunged into boiling water. In some experiments, asparagine, in others, lactic acid, was also added. The experiments were made in duplicate, one series being exposed to, the other protected from, carbon dioxide. Acid, neutral, slightly alkaline, and strongly alkaline starches were investigated: without carbon dioxide, the percentage of maltose obtained varied from traces in the alkaline or neutral, to 10 per cent. in the acid emulsion, but in the presence of carbon dioxide the numbers ranged from 25·56 in the acid emulsion to 39·89 in the strongly alkaline starch.

Asparagine, added in quantities of from 0·4 to 20 per cent. of the starch used, gave rise to an increased production of maltose in the absence of carbon dioxide, which the presence of this gas stimulated in the case of the smallest addition of asparagine, but impeded in the other cases. In all instances, however, the production of maltose was greater with than without asparagine. Lactic acid, added in the proportion of 0·04 per cent. of the starch used, increased the yield of maltose except in the case of the strongly alkaline starch, but in larger quantities, 0·4 per cent., arrested saccharification, but not liquefaction. The presence of carbon dioxide diminished the increments due to the action of lactic acid.

Carbon dioxide only acts favourably when small quantities of amylase are used. D. A. L.

The Function of Peroxides in the Living Cell. IV. Peroxydases. A. Bach and Robert Chodat (*Ber.*, 1903, 36, 600—605. Compare Abstr., 1902, ii, 344 and 522).—Evidence is brought forward that two different substances are concerned in the production of peroxides in the plant and in rendering them active in oxidation. A quantity of horse-radish roots was powdered, kept until the hydrolysis of glucosides was complete, freed from ethereal oil by digesting with 80 per cent. alcohol, and then extracted with 40 per cent. alcohol; the extract was concentrated in a vacuum at 30°, filtered, and precipitated with absolute alcohol. The product was a yellowish-white, gummy mass, exceedingly soluble in water and readily so in 40 per cent. alcohol; it reduced Fehling's solution, but this is not an essential characteristic and can be got rid of by repeatedly dissolving in water and precipitating with alcohol; the purest specimen contained 6 per cent. of ash, including 0·8—1·4 per cent. of aluminium and 0·2 to 0·6 per cent. of manganese, but no iron; when warmed with sodium hydroxide, it yielded ammonia and a base with an odour resembling that

of pyridine, but did not give the proteid reactions. The substance is a very powerful peroxydase, and renders hydrogen peroxide in small quantities very active towards pyrogallol, gallic acid, aniline, dimethylaniline, and *p*-toluidine; larger quantities of hydrogen peroxide render the compound inactive; it also becomes inactive when heated to boiling, but recovers its powers after some hours; further boiling destroys it. It renders active also all the peroxides formed by atmospheric oxidation of organic compounds, such as ether, alcohol, and essential oils. A still more important property is its power of increasing the activity of a peroxide-producing oxydase; in a test experiment, the peroxydase solution caused the absorption by aqueous pyrogallol of only 0·6 c.c. of oxygen, an oxydase solution caused the absorption of 14·1 c.c., but the two together caused an absorption of 19·1 c.c. T. M. L.

Function of Peroxides in the Living Cell. V. Resolution of so-called Oxydases into Oxygenases and Peroxidases. Robert Chodat and A. Bach (*Ber.*, 1903, 36, 606—608).—By fractional precipitation with alcohol of the *Lactarius* oxydase, two fractions were obtained: the first, which was almost insoluble in 40 per cent. alcohol, has very little oxidising power by itself, but in presence of a "peroxydase" becomes a vigorous oxidiser; the last, which is soluble in alcohol, has no oxidising power, but imparts activity to hydrogen peroxide and feeble oxydases; it is thus a true "peroxydase." Most oxydases contain principles of both types, and it is proposed to retain the term peroxydase for those substances (usually containing manganese) which are not themselves oxidisers, but impart activity to, and thus destroy, peroxides, whilst the new term, "*oxygenase*," is proposed for those substances, now isolated for the first time, which are capable of producing hydrogen peroxide, but leave it in an inactive condition. The oxygenases are probably themselves peroxides, and so are very liable to undergo decomposition, whilst the peroxydases are very stable and appear to be present in most vegetable organisms.

T. M. L.

Influence of the Stereochemical Configuration of Glucosides on the Activity of Hydrolytic Diastases. Henri Pottevin (*Ann. Inst. Pasteur*, 1903, 17, 31—51. Compare this vol., ii, 230).—The maltase of blood (horse and rabbit) and of human urine hydrolyses not only maltose (Fischer, *Ber.*, 1895, 28, 1429), but α-methyl-*d*-glucoside.

The following revised classification of the diastases and the glucosides hydrolysed by them is given: invertin; saccharose, raffinose, and gentianose. Maltase; maltose, α-methyl- and α-ethyl-*d*-glucosides, glyceryl-glucoside, trehalose, benzyl-glucoside, and amygdalin. Emulsin; amygdalin, amygdalic nitrile, coniferin, arbutin, picein, salicin, helicin, æsculin, β-methyl-*d*-glucoside, β-glyceryl-glucoside, thymol, and β-carvacrol-glucoside. β-Lactase; lactose, and β-methyl-*d*-galactose. α-Lactase; α-methyl-*d*-galactose. N. H. J. M.

Hydrolysis of Carbohydrates of High Molecular Weight by Soluble Ferments. Émile Bourquelot (*Compt. rend. Soc. Biol.*, 1902, 54, 1140—1143).—Gentianose (Abstr., 1902, i, 744) is only

completely hydrolysed to simple hexoses when invertase and then emulsin, or a mixture of these, is added; emulsin by itself produces very little effect. These facts favour the probability that in the hydrolysis of starch by malt diastase several ferments take part in the reaction, and further show that before concluding that any complex substance simply renders a particular ferment more active, it is necessary to be sure that this substance does not itself contain a ferment capable of acting on some product formed by the action of the ferment which is being studied. A. H.

Proteolytic Enzyme of Yeast. JULIUS SCHÜTZ (*Beitr. chem. Physiol. Path.*, 1903, 3, 433—438).—By the action of the proteolytic enyzme of yeast on euglobulin, pseudoglobulin, crystalline serum albumin, and gelatin products are obtained after eight days which are not precipitable by tannic acid, and are simple decomposition products of peptone; at this time, these substances contain the greater part of the nitrogen of the proteid used.

Pseudoglobulin has some inhibiting influence on the autolytic action of the enzyme on the yeast proteid. Whether the ferment is identical with trypsin is left uncertain. W. D. H.

Some Phosphorus Acid Derivatives of Benzophenone and Methyl Propyl Ketone. CHARLES MARIE (*Compt. rend.*, 1903, 136, 508—510).—By heating together benzophenone and hypophosphorous acid for some days, a homogeneous mixture is obtained; the mass is extracted with hot water and, on addition of lead acetate to the solution, the *lead* salt of an acid of the formula $OH\cdot CPh_2\cdot PO_2H_2$, is precipitated; it is insoluble in water, but soluble in alcohol, acetone, or ether. The free acid, obtained by decomposing the lead salt with hydrogen sulphide, crystallises from water in thin plates, melts at 150—151°, is soluble in all the common organic solvents except ether, and is stable in presence of alkalis, and may be boiled with hydrochloric acid without decomposition. When oxidised with bromine, it gives the hydroxy-phosphinic acid, $OH\cdot CPh_2\cdot PO_3H_2$; this crystallises from water, is soluble in the common organic solvents, and melts at 184—185°. It is a dibasic acid and gives insoluble silver and barium salts.

In the same way, methyl *n*-propyl ketone and hypophosphorous acid give the acid $OH\cdot CMePr^{\alpha}\cdot PO_2H_2$, which was isolated in the form of the lead salt. The acid is a non-crystallisable syrup identical with that already described (this vol., i, 328), is easily oxidised by means of bromine to the hydroxyphosphinic acid, $OH\cdot CMePr^{\alpha}\cdot PO_3H_2$, which melts at 139—140°, is soluble in the common organic solvents except ether, is a dibasic acid, and gives insoluble lead and silver salts. J. McC.

Organic Compounds of Phosphorus with Nitrogen. AUGUST MICHAELIS (*Annalen*, 1903, 326, 129—258).—In the introduction to this paper, an account is given of the compounds of phosphorus and nitrogen, the first of which was obtained by the action of ammonia on phosphorus trichloride by Rose (*Ann. Phys. Chem.*, 1832, 24, 308). A system of nomenclature is suggested in which these substances are

regarded as derived from phosphine, and not, as heretofore, from phosphorous acid; in physical characters, such compounds as $P(OPh)_3$ and $(C_5H_{10}\cdot N)_3P$ closely resemble the phosphines (as PEt_3). Accordingly as phosphorus is directly united with oxygen, nitrogen, or carbon, a compound would be denoted as an *O*-phosphine, an *N*-phosphine, or a *C*-phosphine. Derivatives of phosphorus trichloride, phosphorus oxychloride, &c., which contain chlorine, would be distinguished as *O*-, *N*-, or *C*-chlorophosphines or -oxychlorophosphines; further, the words *primary* and *secondary* would denote whether one or two chlorine atoms are replaced.

Derivatives of Aliphatic Amines.—[With E. MENTZEL.]—Phosphorus trichloride reacts so violently with primary aliphatic amines that only by dilution with low-boiling petroleum can the *N*-chlorophosphines be prepared. *Ethylamine*-N-*chlorophosphine*, $NHEt\cdot PCl_2$, prepared by adding ethylamine (2 mols.) dissolved in petroleum to a similar cooled solution of phosphorus trichloride (1 mol.), is a colourless liquid with a disagreeable aromatic odour, which boils at 92° under 11 mm. and at 222—225° (with decomposition) under the ordinary pressure; it is slowly decomposed by cold water, but is far more stable than phosphorus oxychloride. With increase of the carbon content of the alkyl group, the stability of alkylamine-*N*-chlorophosphines towards water increases. When heated with sulphur under pressure, a small quantity of a thiochlorophosphine is produced, for example, $NHEt\cdot PSCl_2$. *Propylamine*-N-*chlorophosphine*, $NHPr\cdot PCl_2$, boils at 97° under 10 mm. pressure and has a sp. gr. 1·226 at 15°; iso*butylamine*-N-*chlorophosphine* boils at 101° under 10 mm. pressure and has a sp. gr. 1·213 at 15°; *amylamine*-N-*chlorophosphine* boils at 101° under 8 mm. pressure. Secondary *N*-chlorophosphines could not be prepared in a pure state, but the tertiary compounds could be more easily obtained; thus, from *iso*butylamine (6 mols.) and phosphorus trichloride (1 mol.) in solution in petroleum, iso*butylaminechlorophosphine* was prepared as a thick liquid which, however, could not be distilled under diminished pressure. Similarly, from benzylamine, an oily liquid is formed which, on addition of water, is converted into *benzylamine phosphite*, melting at 186°.

[With J. SCHROEMBGENS.]—*Tetrabenzylamine*-N-*phosphonium chloride*, $(CH_2Ph\cdot NH)_4PCl$, is prepared by heating benzylamine hydrochloride (3 mols.) with phosphoric chloride (1 mol.) at 205°, extracting the product with benzene, and recrystallising the residue from alcohol, when it separates in white leaflets melting at 208°, and is converted by alcoholic potassium hydroxide or silver oxide into tribenzylamine-*N*-phosphine oxide, $(CH_2Ph\cdot NH)_3PO$. The *platinichloride*,

$$[(CH_2Ph\cdot NH)_4PCl]_2,PtCl_4,$$

crystallises in long, reddish-yellow needles melting at 200°.

[With TH. SCHALHORN.]—The *N*-chlorophosphines of secondary aliphatic amines are formed when secondary amines are added to phosphorus trichloride, but are best prepared by heating the hydrochlorides of the amine with a large excess of phosphorus trichloride for six hours; from the product, the phosphorus trichloride is distilled, and then the residue distilled under reduced pressure; the *N*-chlorophosphines of this class are liquids or solids with a characteristic

smell, which are decomposed by water and are converted by chlorine into tetrachlorides and by sulphur into thiochlorophosphines. *Diethylamine*-N-*chlorophosphine*, $NEt_2 \cdot PCl_2$, is a clear liquid boiling at 72—75° under 14 mm. and at 189° under the ordinary pressure; it has a sp. gr. 1·196 at 15°. With ethoxyphosphorus chloride, $PCl_2 \cdot OEt$, in ethereal solution, diethylamine forms *diethylamine*-N-*ethoxychlorophosphine*, $NEt_2 \cdot PCl \cdot OEt$, which is a liquid boiling at 90—92° under 13 mm. pressure, is readily decomposed by cold water, and when heated at 170—190° evolves ethyl chloride, leaving a residue which consists of red phosphorus and phosphinediethylamine (m. p. 102°); probably diethylamine-*N*-phosphine oxide, $NEt_2 \cdot PO$ is first formed, which then reacts with the still undecomposed ethoxy-compound. *Dipropylamine*-N-*chlorophosphine*, $NPr_2 \cdot PCl_2$, is an oil boiling at 95° under 11 mm. and at 220—223° under the ordinary pressure; *di*iso*butylamine*-N-*chlorophosphine*, $N(C_4H_9)_2 \cdot PCl_2$, is a crystalline solid melting at 37—38° and boiling at 116—117° under 10 mm. pressure, and readily combines with sulphur at 130—140° producing a thiochlorophosphine; with the diphenol derivative of phosphorus trichloride, di*iso*butylamine forms the phenyl ester, $N(C_4H_9)_2 \cdot P(OPh)_2$, which is a pale yellow oil, not volatile without decomposition. *Diamylamine*-N-*chlorophosphine* is a liquid boiling at 140° under 8 mm. pressure. *Piperidine*-N-*chlorophosphine*, $C_5H_{10}N \cdot PCl_2$, is a liquid boiling at 94—95° under 10 mm. pressure, and is more stable towards water than the other phosphines; *piperidine*-N-*ethoxychlorophosphine*, $C_5H_{10}N \cdot PCl \cdot OEt$, prepared from piperidine and ethoxyphosphorous chloride, is a colourless liquid boiling at 125° under 25 mm. pressure, and is decomposed by heat in the same manner as the diethylamine derivative.

When the N-chlorophosphines are treated with dry chlorine in chloroform solution, they are converted into tetrachlorides, thus, from the propyl derivative, the *compound*, $NPr_2 \cdot PCl_4$, is obtained as a white, crystalline substance which fumes in the air, and yielding the oxychlorophosphine, $NPr_2 \cdot POCl_2$, which is also formed by the action of water. The *di*iso*butylamine* derivative is a similar substance. Additive compounds of these tetrachlorides and phosphoric chloride are produced when the hydrochlorides of secondary amines are treated in chloroform solution with phosphoric chloride; the *compound* from dipropylamine, $NPr_2 \cdot PCl_4, PCl_5$, crystallises in white needles which decompose at 220—221°, and fumes in the air, finally liquefying and forming the oxychlorophosphine; the same reaction takes place violently when the substance is added to water; with dry sulphur dioxide, it yields the oxychlorophosphine, phosphorus oxychloride, and thionyl chloride. The *methyl* compound decomposes at 242—244°; the *ethyl* derivative forms white crystals decomposing at 232—233°; the iso*butyl* derivative decomposes at 168—170°.

[With L. Mottek.]—Secondary N-chlorophosphines of the type $P(NR_2)_2Cl$ have as yet been obtained only in the form of the ethoxy- or phenoxy-derivatives; these are prepared by treating ethoxy- or phenoxy-chlorophosphine with slight excess of the secondary amine in ethereal solution and purifying by distillation under reduced pressure; they are liquids lighter than water and having a strong phosphine-like

odour, and soluble in dilute acids without change, but when these solutions are heated are decomposed into phosphorous acid, dialkylamine, and alcohol; they combine with oxygen, sulphur, and methyl iodide. Secondary *diethylamine-N-ethoxyphosphine*, $P(NEt_2)_2\cdot OEt$, boils at 105—108° under 28 mm. pressure; it combines with sulphur with evolution of heat, forming the *thiophosphine*, $PS(NEt_2)_2\cdot OEt$, which is purified by distilling in steam and then under reduced pressure, and is a yellow oil with an unpleasant odour boiling at 149—151° and stable towards water and dilute acids. With methyl iodide, this compound reacts violently; when diluted with ether, the *phosphonium iodide*, $P(NEt_2)_2\cdot OEt,MeI$, is obtained as an oil which slowly decomposes into diethylamine hydriodide and the *diethylamide* of methylphosphinic acid, $P(NEt_2)_2\cdot OMe$, which is probably formed from the methiodide by the elimination of ethyl iodide; the diamide is a colourless oil with an aromatic odour, boiling at 145—148° under 22 mm. pressure. Secondary *dipropylamine-N-ethoxyphosphine*, $P(NPr_2)_2\cdot OEt$, is a colourless liquid boiling at 143—147° under 29 mm. pressure, and when heated with sulphur gives the *thiophosphine*, $PS(NPr_2)_2\cdot OEt$, which is a yellowish-brown oil with an unpleasant odour boiling at 178—180° under 22 mm. pressure; the corresponding *oxyphosphine*, $PO(NPr_2)_2\cdot OEt$, can be readily obtained by shaking the phosphine with 30 per cent. hydrogen peroxide, and is a colourless oil boiling at 164—166° under 20 mm. pressure. The phosphine combines with methyl iodide, the methiodide being unstable and rapidly changing into the *dipropylamide* of methylphosphinic acid, $P(NPr_2)_2\cdot OMe$; the latter is an oil boiling at 176—180° under 25 mm. pressure. Secondary *piperidine-N-ethoxyphosphine*, $P(C_5H_{10}N)_2\cdot OEt$, boils at 152—154° under 27 mm. pressure; with sulphur, it forms the *thiophosphine*, $PS(C_5H_{10}N)_2\cdot OEt$, which boils at 198—210° under 22 mm. pressure, and with hydrogen peroxide the corresponding *oxide*, $PO(C_5H_{10}N)_2\cdot OEt$, which boils at 176—180° under 20 mm. pressure. With methyl iodide, a stable *phosphonium iodide*, $P(C_5H_{10}N)_2\cdot OEt,MeI$, is obtained; it crystallises in hygroscopic needles, and is converted by silver oxide into the *phosphonium hydroxide*, $P(C_5H_{10}N)_2\cdot OEt,MeOH$; the latter forms slender needles which are faintly alkaline, and does not yield a platinichloride. [With TH. SCHALHORN.]—Secondary *diisobutylamine-N-phenoxyphosphine*,

$$P[N(C_4H_9)_2]_2\cdot OPh,$$

is prepared by the interaction of *iso*butylamine and phenoxyphosphorus chloride in ethereal solution, and is a thick, yellow oil; when heated with methyl iodide at 100°, it is converted into the *compound*, $P[N(C_4H_9)_2]_2MeI$, which crystallises in small needles melting at 132°.

The tertiary N-phosphines are easily prepared from phosphorus trichloride and excess of secondary amines, and are oils which can be distilled, sometimes under the ordinary pressure, and are lighter than water; they dissolve undecomposed in dilute acids, are oxidised by the air, combine readily with sulphur and methyl iodide. *Diethylamine-N-phosphine*, $P(NEt_2)_3$, is a colourless liquid boiling at 80—90° under 10 mm. and at 245—246° (with decomposition) under the ordinary pressure; the *methiodide*, $P(NEt_2)_3,MeI$, is a colourless oil very soluble in water. *Dipropylamine-N-phosphine*, $P(NPr^a{}_2)_3$, boils at 160—165° under 15 mm. and at 310—315° under the ordinary

pressure; the *methiodide* crystallises in white needles melting at 83—84°. *Diiso*propylamine-N-*phosphine*, $P(NPr^{\beta}_2)_3$, is a pale yellow oil boiling at 190—200° under 18 mm. pressure; the *methiodide* crystallises in white needles melting at 138°. *Diiso*butylaminedi-*piperidine*-N-*phosphine*, $C_4H_9N{\cdot}P(C_5H_{10}N)_2$, is obtained as a thick oil by the action of piperidine on the primary di*iso*butylamine-N-chlorophosphine; the *methiodide* is crystalline. Other similar tertiary N-phosphines have been previously described (Abstr., 1895, i, 682; 1898, i, 416).

The primary *N*-oxychlorophosphines are formed when amines act on phosphorus oxychloride in ethereal solution, but are best prepared by heating the amine hydrochloride (1 mol.) with phosphorus oxychloride (2 mols.); the clear liquid which results is distilled under reduced pressure. The *N*-oxychlorophosphines of the primary aliphatic amines are liquids with a disagreeable odour and are decomposed by cold water the more easily the less the number of carbon atoms in the alkyl group. *Methylamine*-N-*oxychlorophosphine*, $NHMe{\cdot}POCl_2$, boils at 132° under 27 mm. pressure and is very unstable towards water; the corresponding *ethylamine* compound boils at 140° under 22 mm. pressure; the *dianilide*, $NHEt{\cdot}PO(NHPh)_2$, is prepared by mixing ethereal solutions of the oxychlorophosphine and aniline, and crystallises in needles melting at 147°; the *phenylhydrazide*,

$$NHEt{\cdot}PO(N_2H_2Ph)_2,$$

melts at 153°. *Propylamine*-N-*oxychlorophosphine*, $NHPr^{\alpha}{\cdot}POCl_2$, boils at 146° under 16 mm. pressure; the *anilide* crystallises in white needles melting at 146°; the *phenylhydrazide* melts at 151°. iso*Butylamine*-N-*oxychlorophosphine* boils at 141° under 14 mm. pressure; the *anilide* melts at 207° and the *phenylhydrazide* at 141°. n-*Amylamine*-N-*oxychlorophosphine* boils at 159° under 17 mm. pressure; the *anilide* melts at 117° and the *phenylhydrazide* at 122°. *Benzylamine*-N-*oxychlorophosphine* could not be obtained quite pure, as it does not distil without decomposing; with benzylamine, it gives the tertiary phosphine oxide, $PO(NH{\cdot}CH_2Ph)_3$; the *phenyl* ester, $CH_2Ph{\cdot}NH{\cdot}PO(OPh)_2$, is prepared by the action of benzylamine on diphenoxyphosphoric chloride, $POCl(OPh)_2$, in benzene solution, and forms stable, white crystals melting at 104—105° and only slowly hydrolysed by alkalis.

The secondary *N*-oxychlorophosphines of the primary aliphatic amines are prepared by mixing phosphorus oxychloride and some excess of the amine in ethereal solution, and, after removing the hydrochloride of the amine by washing the product with water, crystallising the residue from ether; they are also formed by the action of the primary amine on the primary *N*-oxychlorophosphine. Secondary *propylamine*-N-*oxychlorophosphine*, $POCl_2(NHPr^{\alpha})_2$, crystallises in slender needles melting at 88° and is decomposed only slowly by cold water. Secondary iso*butylamine*-N-*oxychlorophosphine* crystallises in white needles melting at 86°. The *phenyl* ester of secondary benzylamine-*N*-oxychlorophosphine, $PO(NH{\cdot}CH_2Ph)_2{\cdot}OPh$, is prepared by the action of benzylamine (4 mols.) on phenoxyphosphoric oxychloride in benzene solution, and crystallises in long needles melting at 114°.

The tertiary *N*-phosphine oxides of the primary aliphatic amines,

which are very easily obtained from the amine and phosphorus oxychloride, are nearly odourless, stable oils. *Propylamine*-N-*phosphine oxide*, $PO(NHPr^{\alpha})_3$, is a thick, nearly colourless liquid; the corresponding iso*butylamine* compound is a waxy, crystalline mass melting at 46—47°; when heated, *iso*butylamine distils and an oxyphosphazo-compound remains. *Tribenzylamine*-N-*oxyphosphine oxide*,

$$PO(NH{\cdot}CH_2Ph)_3,$$

crystallises in long needles melting at 98°.

The primary *N*-oxychlorophosphines of the secondary aliphatic amines (compare Abstr., 1896, i, 344) are prepared by mixing ethereal solutions of the secondary amine and phosphorus oxychloride, or by heating the hydrochloride of the amine with large excess of phosphorus oxychloride; the phosphine is finally distilled under reduced pressure; these compounds have a strong odour resembling camphor or pepper. *Dimethylamine*-N-*oxychlorophosphine*, $NMe_2{\cdot}POCl_2$, is a colourless liquid boiling at 90—91° under 22 mm. and at 194—195° under the ordinary pressure; the *ethyl* ester, $NMe_2{\cdot}PO(OEt)_2$, is prepared by the action of sodium ethoxide in alcoholic solution on the phosphine, and is a liquid of aromatic odour boiling at 85—90° under 5 mm. pressure; the *anilide*, $NMe_2{\cdot}PO(NHPh)_2$, prepared from aniline and *N*-oxychlorophosphine, crystallises in white needles melting at 196°; the *phenylhydrazide*, $NMe_2{\cdot}PO(N_2H_2Ph)_2$, prepared in a similar manner by the use of phenyl hydrazine, forms crystals melting at 194—195°. *Diethylamine*-N-*oxychlorophosphine*, $NEt_2{\cdot}POCl_2$, is a colourless liquid boiling at 100° under 15 mm. and at 220° under the ordinary pressure; [with A. Schall.]—the *ethyl* ester, $NEt_2{\cdot}PO(OEt)_2$, is a colourless, aromatic liquid prepared in similar manner to the corresponding methyl derivative; it boils at 114—117° under 25 mm. and at 218—220° under the ordinary pressure. When this *N*-oxychlorophosphine is treated with potassium cyanide in alcoholic solution, a mixture of the ethyl ester and a *compound*, $NEt_2{\cdot}PO(OEt),HCN$, is obtained; the latter could not be prepared in a pure state. The *phenyl* ester, $NEt_2{\cdot}PO(OPh)_2$, prepared from the *N*-oxychlorophosphine and sodium phenoxide, is a liquid having a sp. gr. 1·1157 at 15°, which, when distilled under reduced pressure, decomposes into triphenyl phosphate and the tertiary diethylaminephosphine oxide. The diphenyl derivative, $NEt_2{\cdot}POPh_2$ (the diethylamide of phenylphosphinic acid), is prepared by the action of sodium on an ethereal solution of diethylamine-*N*-oxychlorophosphine and bromobenzene; it forms colourless crystals melting at 138°, and is converted by concentrated hydrochloric acid into diethylamine and diphenylphosphinic acid (m. p. 190°). The *anilide*, $NEt_2{\cdot}PO(NHPh)_2$, prepared as in the case of the dimethyl derivative, crystallises in slender needles melting at 150°; the *phenylhydrazide* $NEt_2{\cdot}PO(N_2H_2Ph)_2$, forms crystals melting at 184—185°.

[With M. Gmeiner.]—*Dipropylamine*-N-*oxychlorophosphine*,

$$NPr_2{\cdot}POCl_2,$$

is a liquid boiling at 123° under 20 mm. and at 243—244° under the ordinary pressure; the *ethyl* ester boils at 105—110° under 12 mm. pressure and has a sp. gr. 0·975 at 15°; the *anilide* (?) forms white needles melting at 220°; the p-*toluidide* melts at 168°, and the *phenylhydrazide* at 164°, both crystallising in white needles. *Diisobutyl*-

amine-N-*oxychlorophosphine* crystallises in long, flattened needles or plates melting at 54°; the *ethyl* ester is a colourless liquid having a sp. gr. 0·9663 at 14°; the *phenyl* ester forms feathery crystals melting at 56°; the *anilide* crystallises in needles melting at 202°; the p-*toluidide* melts at 180°, and the *phenylhydrazide* at 168°. *Diamylamine*-N-*oxychlorophosphine* is a pale yellow liquid with an aromatic odour, boiling at 150° under 12 mm. pressure and having a sp. gr. 1·0804 at 13° and n_D 1·4648. [With E. KAHNEMANN.]—*Piperidine*-N-*oxychlorophosphine* is a colourless, oily liquid with an odour of peppermint, boiling at 124° under 11 mm. and at 257° under the ordinary pressure, and having a sp. gr. 1·323 at 18° and n_D 1·498; the *ethyl* ester is a liquid and the *phenyl* ester a solid, forming large, colourless prisms melting at 70°; the o-*toluidide* crystallises in rhombic plates melting at 173°. [With W. SCHÜTTE.]—*Tetrachlorohydroquinoline*-N-*oxychlorophosphine*, $C_9NH_{10}\cdot POCl_2$, forms large, monoclinic crystals melting at 79°; the *ethyl* ester boils at 155° under 8 mm. pressure; the *phenyl* ester is a liquid; the *anilide* crystallises in white prisms melting at 176°.

[With E. RATZLAFF.]—The monoethoxy-derivatives of the primary *N*-oxychlorophosphine, $R_2N\cdot POCl\cdot OEt$, are prepared by the action of the secondary amine on ethoxyphosphorus oxychloride (ethyl-*O*-oxychlorophosphine), $OEt\cdot POCl_2$, in the presence of anhydrous ether and purified by distillation under reduced pressure. *Diethylamine*-N-*ethoxyoxychlorophosphine*, $NEt_2\cdot POCl\cdot OEt$, is a colourless liquid with an odour of pepper boiling at 113° under 18 mm. pressure, and is not decomposed by cold water, but is less stable than the *N*-oxychlorophosphines. When heated under the ordinary pressure, it decomposes into ethyl chloride and *phosphinodiethylamine*; the last-mentioned compound, $(NEt_2\cdot PO_2)_3$ or $NEt_2\cdot PO{<}\begin{matrix}O\cdot PO(NEt_2)\\O\cdot PO(NEt_2)\end{matrix}{>}O$, crystallises in needles melting at 103°, and is decomposed by acids into phosphoric acid and the salts of the amine; with phosphoric chloride, it yields diethylamine-*N*-oxychlorophosphine and phosphorus oxychloride; by alcoholic ammonia, it is converted into a *compound*, probably an *aminophosphinic acid*, $NEt_2\cdot PO(OH)\cdot NH_2$, which crystallises in slender needles melting at 144°. *Dipropylamine*-N-*ethoxyoxychlorophosphine* is a liquid which decomposes when an attempt is made to distil it under reduced pressure, forming ethyl chloride and *phosphinodipropylamine*, $(NPr^{\alpha}_2\cdot PO_2)_3$, which is a thick liquid boiling at 240° under 10 mm. pressure. *Diiso*butylamine-N-*ethoxyoxychlorophosphine* also suffers decomposition when heated, and yields, besides ethyl chloride, *phosphinodi*iso-*butylamine*, $N(C_4H_9)_2\cdot PO_2$, which forms crystals melting at 79° and boiling at 255° under 15 mm. pressure.

[With A. SCHALL.]—The bromine compounds corresponding with the *N*-oxychlorophosphines can be prepared by the use of phosphorus oxybromide; they are not volatile without decomposition. *Diethylamine*-N-*oxybromophosphine*, $NEt_2\cdot POBr_2$, is an oily liquid with an odour resembling camphor and decomposed even by cold water; the *propyl* derivative has similar properties. *Diiso*butylamine-N-*oxybromophosphine* crystallises in colourless needles melting at 68°.

The *thiocyano*-compound, $NEt_2\cdot PO(SCN)_2$, is formed when the

N-oxychlorophosphine is heated with silver thiocyanate at 100°, and is a thick, reddish-yellow oil.

The simple derivatives of secondary *N*-oxychlorophosphines and secondary aliphatic amines could not be prepared, although their esters have been obtained; the piperidine derivative and mixed compounds containing an aromatic amine and tetrahydroquinoline are described. [With E. RATZLAFF.]—*Ethyl diethylamine-N-phosphinate*,

$$PO(NEt_2)_2 \cdot OEt,$$

is a colourless liquid with an odour of peppermint, boiling at 140° under 15 mm. pressure, and is soluble in water and immediately decomposed by acids. *Ethyl diethylaminepiperidine-N-phosphinate*, $NEt_2 \cdot PO(C_5NH_{10}) \cdot OEt$, is prepared by the action of piperidine on diethylamine-*N*-ethoxyoxychlorophosphine, and is a liquid of aromatic odour boiling a little higher than the compound last mentioned. [With E. KAHNEMANN.]—*Dipiperidine-N-oxychlorophosphine*, $(C_5NH_{10})_2POCl$, prepared by the action of piperidine on primary piperidine-*N*-oxychlorophosphine, is a crystalline mass boiling at 184° under 12 mm. pressure; [with K. VON AREND] the *ethyl* ester, $PO(C_5NH_{10})_2 \cdot OEt$, prepared from the substance last mentioned and sodium ethoxide, is a yellow liquid boiling at 160—165° under 10 mm. and at 188—192° under 36 mm. pressure, and is soluble in cold dilute acids; the *phenyl* ester is a liquid boiling at 215—216° under 10 mm. pressure; the *anilide*, $(C_5NH_{10})_2PO \cdot NHPh$, crystallises in hexagonal prisms melting at 159°, the o-*toluidide* in needles melting at 146°; the *phenylhydrazide* melts at 155°. [With W. SCHÜTTE.]—*Tetrahydroquinolineaniline-N-oxychlorophosphine*, $NHPh \cdot POCl \cdot C_9NH_{10}$, prepared from aniline and tetrahydroquinoline-*N*-oxychlorophosphine, crystallises in clusters of needles melting at 174—175°, and is converted into the *acid*, $NHPh \cdot PO(C_9NH_{10}) \cdot OH$, which is very unstable when it is dissolved in dilute sodium hydroxide. *Tetrahydroquinoline-o-toluidine-N-oxychlorophosphine* melts at 122°.

[With K. VON AREND.]—The tertiary phosphine oxides, $(R_2N)_3PO$, are formed on oxidation of phosphines and are prepared by prolonged heating under pressure of the primary *N*-oxychlorophosphines with excess of the amine; they are weak bases, soluble in hydrochloric acid and forming mercurichlorides. Mixed tertiary phosphine oxides are very easily prepared by the action of aniline and toluidine on the primary *N*-oxychlorophosphines and have been described above as anilides and toluidides of the latter. Tertiary *diethylamine-N-phosphine oxide*, $PO(NEt_2)_3$, is an oil with aromatic odour, and cannot be distilled, even under reduced pressure; the corresponding derivatives of *dipropylamine* and of *diisobutylamine* are oils. *Tripiperidine-N-phosphine oxide* has been previously described (Abstr., 1895, i, 662, 682), but the hydrochloride and platinichloride do not exist as there stated.

The primary thiochlorophosphines of the primary aliphatic amines are very stable substances, which are easily prepared by mixing the primary amine and phosphorus thiochloride in very dilute ethereal solution or by heating the hydrochloride of the amine with excess of the thiochloride. [With E. MENTZEL.]—*Methylamine-N-thiochlorophosphine*, $NHMe \cdot PSCl_2$, is a colourless or pale yellow liquid with a smell resembling camphor, boiling at 115° under 33 mm.

pressure. [With Fr. Müller.]—The *ethylamine* compound is similar and boils at 105° under 9 mm., at 115° under 20 mm., and at 216° under the ordinary pressure; the *ethyl* ester, $NHEt{\cdot}PS(OEt)_2$, prepared by the action of sodium ethoxide on the last-mentioned substance, is a colourless substance boiling at 94° under 12 mm. pressure; the *phenyl* ester is also liquid. The *anilide*, $NHEt{\cdot}PS(NHPh)_2$, crystallises in needles melting at 106°, the p-*toluidide* melts at 140°, and the *piperidide* at 95°. [With E. Mentzel.]—*Propylamine*-N-*thiochlorophosphine*, $NHPr^{\alpha}{\cdot}PSCl_2$. is a colourless liquid boiling at 121° under 17 mm. pressure; the *ethyl* ester is a pale yellow oil boiling at 98° under 11 mm. pressure and has a sp. gr. 1·005 at 15°; the *anilide* crystallises in slender needles melting at 116°. [With Fr. Müller and E. Mentzel.]—iso*Butylamine*-N-*thiochlorophosphine* is a colourless liquid boiling at 116° under 9 mm., at 123° under 15 mm., and at 251° under the ordinary pressure; the *ethyl* ester boils at 104° under 12 mm. pressure; the *anilide* forms slender needles melting at 118°; the p-*toluidide* melts at 152°, the *piperidide* at 106°, and the *phenylhydrazide* at 129°. [With E. Mentzel.]—n-*Amylamine*-N-*thiochlorophosphine* is a pale yellow liquid boiling at 140° under 16 mm. pressure; the p-*toluidide* crystallises in slender needles melting at 129°. [With J. Schrömbgens.]—*Benzylamine*-N-*thiochlorophosphine*,

$$CHPh{\cdot}NH{\cdot}PSCl_2,$$

which is a pale yellow oil, cannot be completely purified as it is not volatile, even under reduced pressure; the *monophenyl* derivative, $CH_2Ph{\cdot}NH{\cdot}PSCl{\cdot}OPh$, was prepared.

The secondary thiochlorophosphines of the primary aliphatic amines could only be obtained in the form of esters. The *diphenyl* ester of secondary dibenzylamine-*N*-thiophosphine (phenyl dibenzylamine-*N*-thiophosphinate), $PS(NH{\cdot}CH_2Ph)_2{\cdot}OPh$, is prepared by the action of benzylamine (4 mols.) on a benzene solution of phosphorus thiochloride (1 mol.), $OPh{\cdot}PSCl_2$; the ester crystallises in white needles melting at 73°.

The tertiary *N*-phosphine sulphides of primary aliphatic amines are very readily prepared by the action of excess of the primary amines on phosphorus sulphochloride, and are very stable substances. [With Fr. Müller.]—Tertiary *ethylamine*-N-*phosphine sulphide*, $PS(NHEt)_3$, forms white, monoclinic crystals melting at 68°; it does not react either with methyl iodide or acetic anhydride. The corresponding *propylamine* derivative crystallises in long needles melting at 73°; the iso*butylamine* derivative in monoclinic crystals melting at 78·5°; on distillation, the latter is converted into the thiophosphazo-compound, $P_2S_2(C_4H_9N)_2(NHC_4H_9)_2$. The *phosphine sulphide*, $C_4H_9{\cdot}NH{\cdot}PS{\cdot}NHEt$, prepared by the action of *iso*butylamine on ethylaminethiochlorophosphine, crystallises in small leaflets melting at 48·5°. *Amylamine*-N-*phosphine sulphide* is a thick, oily liquid. [With J. Schrömbgens.]—*Tribenzylamine*-N-*phosphine sulphide* crystallises in long needles melting at 127°.

The primary *N*-thiochlorophosphines of the secondary aliphatic amines are prepared from the secondary amine and phosphorus thiochloride, using, however, in this case, less diluent than with the class of phosphines just described; they are also prepared from the hydrochloride of the amine; they are purified by distillation under

reduced pressure and converted into the corresponding oxychlorophosphines by treatment with mercuric oxide in benzene solution. *Dimethylamine-N-thiochlorophosphine*, $NMe_2 \cdot PSCl_2$, is a colourless liquid boiling at 85—90° under 16 mm. pressure; the *ethyl* ester,

$$NMe_2 \cdot PS(OEt)_2,$$

prepared in the same manner as the corresponding oxygen compound, is a colourless liquid boiling at 107° under 45 mm. pressure; the *anilide*, $NMe_2 \cdot PS(NHPh)_2$, crystallises in colourless needles melting at 209—210°. [With R. Hülsberg.]—*Diethylamine-N-thiochlorophosphine*, $NEt_2 \cdot PSCl_2$, is a colourless liquid boiling at 107° under 14 mm. pressure and having a sp. gr. 1·105 at 15°; the *ethyl* ester boils at 110° under 20 mm. pressure and has a sp. gr. 1·0056 at 15°; the *phenyl* ester forms crystals melting at 70°; the *anilide* crystallises in white needles melting at 192°; the p-*toluidide* in needles melting at 166—167°; the *dipiperidide* in hexagonal prisms melting at 126°, and the *phenylhydrazide* in cubic forms. *Dipropylamine-N-thiochlorophosphine*, $NPr_2 \cdot PSCl_2$, is a liquid boiling at 132—134° under 15 mm. and at 240—245° (with decomposition) under the ordinary pressure; it has a sp. gr. 1·077 at 15°; the *anilide* crystallises in leaflets melting at 145° and the *phenylhydrazide* at 196°. *Diisobutylamine-N-thiochlorophosphine*, $N(C_4H_9)_2 \cdot PSCl_2$, crystallises in leaflets melting at 36° and boiling at 150° under 10 mm. pressure; the *diamylamine* derivative is an oil boiling at 160—163° under 13 mm. pressure and has a sp. gr. 1·0288 at 15°; its *methyl* ester is a yellow oil boiling at 118—121° under 13 mm. pressure and has a sp. gr. 1·0024 at 15°; the *phenyl* ester crystallises in needles melting at 64°; the *anilide* melts at 141°. [With O. Steinkopf.]—*Piperidinethiochlorophosphine*, $C_5NH_{10} \cdot PSCl_2$, purified by distilling with steam, is an oil with an odour of camphor; it boils at 146—149° under 21 mm. pressure and has a sp. gr. 1·3092 at 15°; the *ethyl* ester is an oily liquid boiling at 138° under 10 mm. pressure and has a sp. gr. 1·0433 at 16°; the *anilide* forms needles melting at 199°; the p-*toluidide* melts at 190°, and the *phenylhydrazide*, which crystallises in needles, at 158°.

[With M. Pape.]—The *N*-thiobromophosphines are prepared in a manner similar to that used for the *N*-thiochlorophosphines; they cannot be distilled under reduced pressure. *Diethylamine-N-thiobromophosphine*, $NEt_2 \cdot PSBr_2$, is a pale yellow liquid; the *dipropylamine* derivative is also liquid; the *diisobutylamine* compound crystallises in white leaflets melting at 66°.

[With O. Steinkopf.]—The secondary *N*-thiochlorophosphines of the secondary aliphatic amines are difficult to prepare. Secondary *piperidine-N-thiochlorophosphine*, $PSCl(C_5NH_{10})_2$, crystallises in rhombic prisms melting at 98°; the *ethyl* ester is a yellow liquid boiling at 191° under 10 mm. pressure and has a sp. gr. 1·0633 at 16°; the *phenyl* ester crystallises in long needles melting at 108°, the *anilide* in needles melting at 112°, and the *toluidide* at 157°.

The tertiary *N*-phosphine sulphides of secondary aliphatic amines are prepared in the same manner as the analogous *N*-phosphine oxides; they are colourless liquids which cannot be distilled under reduced pressure. Tertiary *diethylamine-N-phosphine sulphide*, $PS(NEt_2)_3$, is a colourless oil; the *diisobutylamine* derivative, which has a sp. gr.

0·9965 at 15°, and the mixed compound, $PS[N(C_4H_9)_2]_2{\cdot}NEt_2$, which has a sp. gr. 1·0023 at 15°, were obtained. The *piperidine* compound crystallises in leaflets melting at 120° (the crystals have been measured).

Derivatives of Aromatic Amines.—The primary chlorophosphines of the secondary aromatic amines were prepared in the usual manner and are liquids of disagreeable odour, very readily decomposed by moisture. [With S. DANZIGER.]—*Methylaniline*-N-*chlorophosphine*, $NMePh{\cdot}PCl_2$, is a pale yellow liquid boiling at 138—140° under 10 mm. and at 251° under the ordinary pressure; with chlorine, it forms a tetrachloride, which is a pale yellow, crystalline mass decomposed by water into the oxychlorophosphine; with sulphur, the dichloride yields a thiochlorophosphine. [With J. OTTENS.]—*Ethylaniline*-N-*chlorophosphine* boils at 143° under 12 mm. pressure. [With H. WENNCKES.]—Diphenylamine and phosphorus trichloride only react when heated together at a high temperature, and form a compound, $NPh_2{\cdot}PO$, which crystallises in needles from water with H_2O; it melts at 224°; the same compound is formed by the interaction of phosphoric chloride and diphenylamine.

[With S. NATHANSON.]—The primary *N*-oxychlorophosphines of primary aromatic amines are prepared by the action of phosphorus oxychloride on the hydrochlorides of the primary aromatic amines; the corresponding acids, $C_6H_4Cl{\cdot}NH{\cdot}PO(OH)_2$, are only stable when chlorine is present in the phenyl nucleus. Aniline-*N*-oxychlorophosphine, $NPh{\cdot}POCl_2$, and the corresponding phenyl ester chloride, $NPh{\cdot}POCl{\cdot}OPh$ (Abstr., 1894, i, 128, 588), are here described in greater detail; by treating the latter with dilute alkali, it is converted into the *monophenyl* ester of aniline-*N*-phosphinic acid,

$$NHPh{\cdot}PO(OPh){\cdot}OH,$$

which crystallises in colourless leaflets melting at 134°; the *silver* salt is a white precipitate; the *phenyl ethyl ester*, $NHPh{\cdot}PO(OEt){\cdot}OPh$, is formed when an alcoholic solution of the ester chloride is evaporated, and crystallises in needles melting at 120°. *m*-Tolyl phenyl aniline-*N*-phosphinate, $NHPh{\cdot}PO(OPh){\cdot}O{\cdot}C_6H_4Me$, is formed by the action of sodium *m*-tolyloxide on the ester chloride in benzene solution.

[With W. HEINRICI.]—Of the substances containing chloroanilines (compare Abstr., 1895, i, 364), the 2 : 4-*dichloroaniline*-N-*oxychlorophosphine*, $C_6H_3Cl_2{\cdot}NH{\cdot}POCl_2$, which is prepared by heating the hydrochloride of 2 : 4-dichloroaniline with phosphorus oxychloride at 145°, forms crystals melting at 126° and is converted by dilute alkalis into the salts of 2 : 4-*dichloroanilinephosphinic acid*, $C_6H_3Cl_2{\cdot}NH{\cdot}PO(OH)_2$, which crystallises in small, thick prisms melting at 167°; the *copper* salt is a bluish-green powder; the *ethyl* ester, produced when the oxychlorophosphine is warmed with alcohol, forms needles melting at 106°; the *phenyl* ester, prepared in a similar manner by the use of phenol, crystallises in needles melting at 132°; the p-*tolyl* ester melts at 162°. [With LEO ASCHNER.]—s-*Trichloroaniline*-N-*oxychlorophosphine*,

$$C_6H_2Cl_3{\cdot}NH{\cdot}POCl_2,$$

prepared by prolonged heating of *s*-trichloroaniline and phosphorus oxychloride, forms crystals melting at 128° and is converted by alkalis into the salts of the corresponding phosphinic acid, which cannot,

however, be isolated. [With E. SILBERSTEIN.]—p-*Bromoaniline*-N-*oxychlorophosphine* forms cubic crystals melting at 98°; the corresponding *phosphinic acid* forms soft scales melting at 158°; the *phenyl* ester crystallises in plates melting at 112°; the *monophenyl* ester is prepared from the ester chloride and is a crystalline powder melting at 164°; the p-*tolyl* ester crystallises in needles melting at 138°, and the corresponding *acid ester* in plates melting at 230°; the *dipiperidide*, $C_6H_4Br\cdot NH\cdot PO(C_5NH_{10})$, prepared from piperidine and the oxychloride, forms aggregates of needles melting at 169°. m-*Bromoaniline*-N-*oxychlorophosphine*, $C_6H_4Br\cdot NH\cdot POCl_2$, melts at 87°; the *β-naphthyl* ester, prepared from this substance and β naphthol, crystallises in needles melting at 166·5°; the *piperidide* forms cubic crystals. [With LEO ASCHNER.]—2 : 4-*Dibromoaniline*-N-*oxychlorophosphine* forms crystals melting at 134°; the *N*-phosphinic acid obtained from it yields a *copper* salt as a green, insoluble powder; the *ethyl* ester crystallises in leaflets melting at 114°; a *potassium* salt of an acid ester has been obtained crystallising in leaflets; the *phenyl* ester forms needles melting at 141°; the p-*tolyl* ester melts at 158°; the *anilide* crystallises in needles melting at 228°; the *toluidide* melts at 214° and the *piperidide* at 186°. s-*Tribromoaniline*-N-*oxychlorophosphine*,

$$C_6H_2Br_3\cdot NH\cdot POCl_2,$$

crystallises in needles melting at 148°. The *N*-oxychlorophosphines, obtained from *m*- and *p*-nitroanilines, crystallise in needles. [With O. STREBEL.]—The m-*nitro*-derivative melts at 94°; its *ethyl* ester forms needles melting at 120°; the *anilide* melts at 177°; the p-*nitro*-derivative melts at 156° and its *anilide* at 242°; the *o*-nitro-compound could not be obtained. [With S. NATHANSON.]—The *phenyl* ester chloride of *p*-toluidine-*N*-phosphinic acid, $C_6H_4Me\cdot NH\cdot POCl\cdot OPh$, is prepared from *p*-toluidine-*N*-oxychlorophosphine (Abstr., 1894, i, 128) and crystallises in small spikes melting at 77°. 3-*Bromo*-p-*toluidine*-N-*oxychlorophosphine* crystallises in short, thick prisms and is very easily converted by alkalis into salts of [with W. HEINRICI] 3-*bromo*-p-*toluidine*-N-*phosphinic acid*, $C_6H_3BrMe\cdot NH\cdot PO(OH)_2$, which crystallises in small prisms melting at 142°; the *copper* salt is a green powder; the *ethyl* ester forms long needles melting at 102°; the *potassium* salt of the monoethyl ester was prepared and crystallised in leaflets; the *phenyl* ester, crystallising in long needles, melts at 126° and the *tolyl* ester at 154°. [With W. HERBST.]—Of the xylidine derivatives, m-*xylidine*-N-*oxychlorophosphine*, $C_6H_3Me_2\cdot NH\cdot POCl_2$, crystallises in white needles or cubes melting at 79°; the *ethyl* ester melts at 96°, and the *phenyl* ester at 115°. The p-*xylidine* compound forms needles melting at 119°, and the o-*derivative*, which is very difficult to prepare, forms needles melting at 76°. [With J. HÖFKER.]—*ψ-Cumidine*-N-*oxychlorophosphine* melts at 122° and the *mesidine* derivative at 155°.

[With K. VON AREND.]—*N*-Oxychlorophosphines are obtained by the action of phosphoric chloride on *m*- and *p*-aminobenzoic acids. In the absence of a solvent, the anhydride of the acid is formed, but in the presence of chloroform the N-*oxychlorophosphine*,

$$COCl\cdot C_6H_4\cdot NH\cdot POCl_2,$$

is produced; it crystallises in prisms melting at 109—110° and is

decomposed by water into the phosphate of *m*-aminobenzoic acid. *Ethyl* m-*aminobenzoate*-N-*phosphinate*, $CO_2Et\cdot C_6H_4\cdot NH\cdot PO(OEt)_2$, prepared by the action of alcohol on the compound last mentioned, is an oil boiling at 135° under 35 mm. and at 232—234° under the ordinary pressure; the corresponding *methyl* ester, prepared by use of methyl alcohol, is a colourless liquid boiling at 184—186°. Phosphoric chloride acts more slowly on *p*-aminobenzoic acid than on the *m*-acid, producing the N-*oxychloride*, which crystallises in prisms of little stability melting at 168°; by water, it is hydrolysed, the phosphate of *p*-aminobenzoic acid being formed. The *methyl* ester boils at 166—167° and the *ethyl* ester at 113—118° under 45—50 mm. and at 206—207° under the ordinary pressure.

Secondary *N*-oxychlorophosphines of aromatic amines, $(NHAr)_2POCl$, and the corresponding monobasic *N*-phosphinic acid, $(NHAr)_2PO(OH)$, have been previously prepared (compare Abstr., 1885, 1134; 1894, i, 588; also Autenrieth and Rudolph, *ibid.*, 1900, i, 570); details are here given of the preparation in quantity of dianiline-*N*-oxychlorophosphine and the corresponding phosphinic acids. [With R. Securius.]—*Ethyl dianiline*-N-*oxyphosphinate*, $PO(NHPh)_2\cdot OEt$, prepared by adding an alcoholic solution of the oxychlorophosphine to sodium ethoxide, or from ethoxyphosphorus oxychloride and aniline, crystallises in plates melting at 114°; the *phenyl* ester was also prepared by two methods analogous to those just described, and also by heating oxyphosazobenzeneanilide, $NPh\!:\!PO\cdot NHPh$, with phenol; when prepared from the *N*-oxychloride, the substance, which crystallises in needles, melts at 169°, whereas that obtained from phenol phosphoric chloride melts at 179·5°. p-*Chlorophenyl dianiline*-N-*phosphinate*, $PO(NHPh)_2\cdot O\cdot C_6H_4Cl$, melts at 167—168°. *Ethyl di*-p-*toluidine*-N-*phosphinate*, $PO(NH\cdot C_6H_4Me)_2\cdot OEt$, crystallises in prisms melting at 108°. *Phenyl aniline*-p-*toluidine*-N-*phosphinate*,

$$C_6H_4Me\cdot NH\cdot PO(NHPh)\cdot OPh,$$

crystallises in needles melting at 136—137°. *Ethyl di*-o-*toluidine*-N-*phosphinate*, prepared from the corresponding oxychlorophosphine, crystallises in needles melting at 115°; the *phenyl* ester forms prisms melting at 157·5°.

Many tertiary *N*-oxyphosphines (the anilides of orthophosphoric acid) have been prepared (compare Autenrieth and Rudolf, *loc. cit.*). [With W. Herbst.]—*Tri*-m-*xylidine*-N-*phosphine oxide*,

$$PO(NH\cdot C_6H_3Me_2)_3,$$

prepared from *m*-xylidine and phosphorus oxychloride, forms slender needles melting at 198° and yields a nitro-derivative, which crystallises in reddish-brown needles; the para-*compound* melts at 247°; the ortho-*compound* crystallises in rhombic prisms melting at 183°; the *ψ-cumidine* compound forms needles melting at 217°, and the *mesidine* derivative melts at 240°.

[With S. Danziger.]—Of the primary *N*-oxychlorophosphines of secondary amines (aromatic and aromatic-aliphatic), diphenylamine-*N*-oxychlorophosphine, $NPh_2\cdot POCl_2$, has been described. *Methylaniline*-N-*oxychlorophosphine*, $NPhMe\cdot POCl_2$, is a yellow liquid boiling at 150—151° under 10 mm. and at 282° under the ordinary

pressure; by treatment with ammonia, it is converted into *methylaniline-N-aminophosphinic acid*, $NPhMe\cdot PO(OH)NH_2$, which formed leaflets melting at 125°. The esters derived from this oxychlorophosphine are unstable; the *phenyl* ester crystallises in needles melting at 50°. The *anilide*, $NPhMe\cdot PO(NHPh)_2$, forms white needles melting at 192°; the *toluidide* melts at 232°, the *piperidide* at 86°, and the *phenylhydrazide* at 148°. [With J. OTTENS.]—*Ethylaniline-N-oxychlorophosphine*, $NPhEt\cdot POCl_2$, is a colourless liquid boiling at 159° under 16 mm. pressure.

The secondary *N*-oxychlorophosphines of secondary anilines can only be obtained as mixed compounds, as *aniline-ethylaniline-N-oxychlorophosphine*, $NPhEt\cdot PO(NHPh)Cl$, prepared from ethylaniline-*N*-oxychlorophosphine and aniline, forms prisms melting at 113°. [With S. DANZIGER.]—As an example of the tertiary phosphine oxides, *methylaniline N-phosphine oxide*, $PO(NPhMe)_3$, which crystallises in needles melting at 162°, and *ethylaniline-N-phosphine oxide*, $PO(NPhEt)_3$, melting at 182°, are described.

[With J. OTTENS.]—The thiochlorophosphines of primary aromatic amines cannot be prepared, but the derivatives of secondary anilines are easily obtained by heating the corresponding chlorophosphine with sulphur. *Methylaniline-N-thiochlorophosphine*, $NPhMe\cdot PSCl_2$, is a yellow liquid having a sp. gr. of 1·357 at 22°; the corresponding *ethylaniline* derivative is similar; it yields a liquid *ethyl* ester, an *anilide* melting at 140°, and a *toluidide* melting at 158°.

Tertiary phosphine sulphides are readily prepared. K. J. P. O.

Organo-mercury Compounds of Salicylic Acid. G. BURONI (*Gazzetta*, 1902, 32, ii, 305—311).—By treating yellow mercuric oxide, suspended in water, with salicylic acid, a compound known as basic or secondary mercury salicylate is obtained, in which the mercury is regarded as replacing both the hydrogen of the hydroxyl group and that of the carboxyl. The author shows, however, that this compound is the anhydride of a hydroxymercurisalicylic acid and has the constitution $OH\cdot C_6H_3{<}{\overset{Hg}{\underset{CO}{}}}{>}O$; an improved method of preparation is given. On treating the anhydride with ammonium carbonate, *ammonium hydroxymercurisalicylate* is obtained, which has a caustic reaction.

Chloromercurisalicylic acid, $HgCl\cdot C_6H_3(OH)\cdot CO_2H$, prepared by the action of acetic acid on the corresponding sodium or calcium salt, separates from alcohol in mammillary aggregates of needles. The *lithium* and *calcium* salts were prepared and analysed.

Bromomercurisalicylic acid, $C_7H_5O_3BrHg$, and *iodomercurisalicylic acid* crystallise from alcohol in colourless, mammillary masses.

T. H. P.

Organic Chemistry.

Catalytic Decomposition of Ethyl Alcohol by Finely-divided Metals; Regular Formation of Aldehyde. Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1903, **136**, 738—741).—At 500°, ethyl alcohol begins to decompose, yielding, on the one hand, ethylene and water, and on the other aldehyde and hydrogen; but secondary reactions also take place, acetylene, ethane, benzene, and naphthalene being formed as well as carbon mono- and di-oxides (Berthelot, *Traité de Chimie organique*, 1872, p. 164). Jahn (Abstr., 1880, 794) found that in the presence of zinc dust ethyl alcohol decomposed into ethylene and water at 300—350°, and Ipatieff (Abstr., 1901, i, 248; 1902, i, 4, 335) showed that at 600° aldehyde and hydrogen were formed in the presence of zinc and litharge; under the influence of other substances, ethylene and water were produced.

When ethyl alcohol is passed over heated reduced copper, a reaction begins at 200° and is very vigorous at 250°, the alcohol being decomposed exclusively into aldehyde and hydrogen. Up to a temperature of 300°, the same change occurs, and at this temperature as much as half the alcohol is decomposed. At 420°, the gas evolved consists of equal volumes of methane (12·5 per cent.) and carbon monoxide (12·5 per cent.), together with hydrogen (75 per cent.); it was ascertained that the two gases first mentioned are formed at the expense of the aldehyde, which, in the presence of reduced copper, begins to decompose at 400°.

In the case of reduced nickel, decomposition of the alcohol begins at 150°, and is rapid at 170°; from a given quantity of alcohol, the evolution of gas per minute is, at 178°, 8 c.c.; at 210°, 24 c.c.; at 250°, 95 c.c.; and at 325°, 74 c.c. At 178°, some aldehyde is formed, but part (somewhat less than a half) is already destroyed; the composition of the gas evolved at this temperature is: CO, 23; CH_4, 29; and H_2, 48 percent.; the excess of methane over carbon monoxide is due to the fact that the latter is partly converted into the former by hydrogen in the presence of nickel (Abstr., 1902, i, 333). At 230°, decomposition of the carbon monoxide into carbon dioxide and carbon begins (Abstr., 1902, ii, 317); this decomposition and the hydrogenation of the carbon monoxide are both very rapid at 300°, and accordingly the volume of gas evolved decreases. At 330°, the gas consists of carbon dioxide, 19·5; methane, 60·7; and hydrogen, 19·8 per cent.; no aldehyde was obtained.

Reduced cobalt acts in just the same manner as nickel, but the secondary decomposition of the carbon monoxide begins at a somewhat higher temperature.

Spongy platinum only begins to decompose the alcohol at 270°, the action increasing regularly with the temperature; at 310°, the gas evolved consists of carbon monoxide, 30; methane, 30; and hydrogen, 40 per cent. Only a small quantity of aldehyde was collected, as three-fourths had been destroyed in producing the methane and carbon monoxide. K. J. P. O.

Action of Hydrogen Bromide on Nitro*iso*butyl Glycol. NICOLAUS I. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 23—26). —By the action of hydrogen bromide on nitro*iso*butyl glycol, the hydroxyl groups are not replaced by bromine, but a *compound*, $C_8H_{13}O_4NBr_2$, is obtained which crystallises from alcohol in large, rhombic plates melting at 115—116°; it is a neutral substance, is readily soluble in methyl alcohol or ethyl acetate, and has the normal molecular weight in freezing acetic acid; it contains no hydroxyl groups, and when treated with potassium hydroxide, one of the bromine atoms is removed as hydrogen bromide with much greater readiness than the other, the resulting *compound*, $C_8H_{12}O_4NBr$, which crystallises from alcohol in colourless plates, melts at 78° and is readily oxidised by permanganate; reduction with sodium and alcohol gives the amino-*iso*butyl glycol obtained by Piloty and Ruff (Abstr., 1897, i, 586) by the reduction of nitro*iso*butyl glycol. T. H. P.

Nitrates of Mannitol and Dulcitol. JOHN H. WIGNER (*Ber.*, 1903, 36, 794—800).—Contrary to the statement of Tichanowitsch (*Zeit. Chem.*, 1864, 482), dulcitol hexanitrate is not decomposed by prolonged heating at 40°, and mannitol hexanitrate, whether wet or dry, is only very slowly decomposed at 100°, the melting point falling one degree in 15 minutes and four degrees in 45 minutes.

Mannitol pentanitrate can be prepared by direct nitration of mannitol, but is always mixed with the hexanitrate; a separation was effected by diluting the nitration mixture until most of the hexanitrate was precipitated and then evaporating and again diluting. The best method of preparing the pentanitrate is, however, by dissolving the hexanitrate in alcohol, adding pyridine (in place of the ammonia used by Tichanowitsch), and boiling for an hour; the pyridine is removed by pouring into water, extracting with ether, and washing the ether with water; the product, when recrystallised, melts at 81—82° (Tichanowitsch gave 79°), dissolves in 3000 parts of water at 15°, has a normal molecular weight, and crystallises unchanged from acetyl chloride.

Dulcitol pentanitrate, prepared by a similar method and recrystallised three times from alcohol and water, sinters at 71° and melts at 75°; like mannitol pentanitrate, it has a bitter taste and strong physiological action. T. M. L.

Preparation of some Mixed Ethers of Tertiary Alcohols. K. LAZINSKY and W. SWADKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 100—103).—*Methyl* ter.-*butyl ether*, $CMe_3{\cdot}OMe$, obtained together with *iso*butylene by the action of a methyl alcoholic solution of potassium hydroxide on *ter.*-butyl chloride, is a mobile liquid with a characteristic odour resembling that of camphor; it boils at 53—54° and has the sp. gr. 0·7642 at 0°.

Ethyl *ter.*-butyl ether may be prepared in the same way.

T. H. P.

Methyl Sulphate as an Alkylating Agent. FRITZ ULLMANN (*Annalen*, 1903, 327, 104 119. Compare Abstr., 1900, i, 619).—Methyl sulphate is best prepared by bringing together methyl alcohol

(27 grams) and chlorosulphonic acid (100 grams) at $-10°$ and then distilling the mixture under 20 mm. pressure at a temperature of 140°; the yield amounts to 80—83 per cent. of the theoretical. The use of Nordhausen sulphuric acid only gives a yield of 42 per cent. (D.R.-P. 113239).

The interaction of methyl sulphate and aromatic amines does not follow the course described by Claesson and Lundvall (Abstr., 1881, 240); 2 mols. of the base react with 1 mol. of the ester, yielding the salt of methyl hydrogen sulphate and a secondary methylamine, thus: $SO_4Me_2 + 2R \cdot NH_2 = R \cdot NH_2, MeHSO_4 + R \cdot NHMe$. When methyl sulphate is added to an ethereal solution of aniline, heat is developed, a precipitate of aniline methyl sulphate is formed, and a mixture of methylaniline and a smaller amount of dimethylaniline is produced in the solution. Both *o*- and *p*-toluidine behave in a similar manner. The same reaction takes place when the suspension of the bases in water is shaken with methyl sulphate; the yield is better with the higher homologues of aniline than with aniline. By this means were prepared *nitrosomethyl*-m-*xylidine* and *nitrosomethylmesidine*, both of which are yellow oils. *Monomethylmesidine* is a liquid boiling at 228—229° under 739 mm. pressure.

When dimethylanilines are heated with methyl sulphate in benzene solution, ammonium bases are formed and isolated as salts of methyl hydrogen sulphate; thus, from dimethyl-*o*-toluidine, *trimethyl*-o-*tolylammonium methyl sulphate* is obtained, and from dimethyl-*p*-toluidine, *trimethyl*-p-*tolylammonium methyl sulphate*, which crystallises in hygroscopic scales.

From *m*-nitroaniline, both the monomethyl and the dimethyl derivatives can be easily prepared; from *p*-nitroaniline, monomethyl-*p*-nitroaniline was obtained in the form of its nitroso-derivative (m. p. 104°). When dimethylaminoazobenzene is heated with methyl sulphate in nitrobenzene solution, the ammonium compound is formed and isolated in the form of its iodide. From diphenylamine, methyldiphenylamine is readily obtained.

Phenols are extremely easily methylated by shaking their alkaline solutions with the calculated quantity of methyl sulphate; thus, from phenol, 96 per cent. of the theoretical amount of the methyl ether is obtained. *o*- and *p*-Nitrophenols gave equally good results. The three dihydroxybenzenes were methylated in the same manner. Pyrogallol gives an excellent yield of the trimethyl ether. Both α- and β-naphthols and 2 : 7-dihydroxynaphthalene can be methylated in this way.

The aromatic (benzene and naphthalene) sulphonic acids can be converted into their methyl esters by adding a benzene solution of methyl sulphate to their dry sodium salts.

Quinoline and quinaldine are both quantitatively converted into their ammonium bases by treatment with methyl sulphate in benzene solution; both salts form hygroscopic crystals. *Phenylmethylacridinium methyl sulphate* is prepared by adding methyl sulphate to a solution of phenylacridine in nitrobenzene, and forms yellow leaflets, dissolving in alcohol with a yellow colour and a green fluorescence. In a similar manner, *methyl* 2 : 3-*diaminophenazonium nitrate* was obtained; it crys-

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tallises in large, dark green, lustrous needles, and dissolves in alcohol to an orange-yellow solution with a green fluorescence. K. J. P. O.

Solubility of Sodium Acetate in Water and Alcohol. GUIDO SCHIAVON (*Gazzetta*, 1902, **32**, ii, 532—535).—Tables are given of measurements of the solubility of crystallised sodium acetate, at various temperatures, in water, and of the anhydrous salt in alcohol of different strengths. T. H. P.

Compounds of Plumbic Acid with Organic Acids. ALBERT COLSON (*Compt. rend.*, 1903, **136**, 675—677).—The preparation of lead tetra-acetate and tetrapropionate by the action of acetic and propionic acids on red lead is described. [No reference is made to the prior work of Hutchinson (Trans., 1893, **63**, 1136), and Hutchinson and Pollard (Trans., 1896, **69**, 212) on this subject.]

With the butyric acids, *lead tetrabutyrates*, $Pb(C_4H_7O_2)_4$, are obtained. J. McC.

Action of Metals at High Temperature on Fatty Acids. ALEXANDRE HÉBERT (*Compt. rend.*, 1903, **136**, 682—684).—It has already been shown (Abstr., 1901, i, 251) that at a high temperature zinc acts on saturated fatty acids giving carbon dioxide, water, hydrogen, and hydrocarbons of the olefine series. It has now been found that the easily oxidisable metals, sodium, magnesium, aluminium, zinc, iron, and tin, react with saturated fatty acids at 350° giving the same products as have already been noticed. The hydrocarbons obtained from stearic acid are those containing from 22 to 28 carbon atoms in the molecule. Copper, silver, and the heavy metals do not cause this decomposition.

A similar decomposition takes place with unsaturated acids: thus, oleic acid and zinc powder give for the most part the hydrocarbon $C_{18}H_{38}$. Lauric acid gives hydrocarbons with C_8, C_{20}, and C_{26}.

It has been proved that during the action a ketone is first formed (stearone was isolated), and this, at the high temperature, loses carbon dioxide and gives the hydrocarbons which have been found. J. McC.

Chemistry of Brown-Coal-Tar. THEODOR ROSENTHAL (*Zeit. angew. Chem.*, 1903, **16**, 221—222. Compare Abstr., 1901, i, 581).—The liquor which is obtained from brown-coal in the "*Schwel-prozess*" contains acetic, propionic, butyric, and valeric acids. Probably hexoic and undecoic acids are also present, but not *iso*butyric acid. The presence of catechol was also demonstrated. K. J. P. O.

Hydrolysis of Organic Peroxides and Peracids. A. M. CLOVER and G. F. RICHMOND (*Amer. Chem. J.*, 1903, **29**, 179—203).—Acetic peroxide may be obtained in nearly theoretical yield by the action of barium dioxide on an ethereal solution of acetic anhydride at 0°. Its solubility in water at 25° is 54·2 grams per litre. The aqueous solution gradually suffers hydrolysis with formation of

molecular proportions of acetic and peracetic acids; in a 5 per cent. solution, the change is complete in 48 hours. The peracetic acid slowly changes into acetic acid and hydrogen peroxide; at the end of a month, nearly the whole of the active oxygen is present in the latter form. If a solution of acetic peroxide is left for 24 hours, the unchanged peroxide is then extracted with light petroleum, and the aqueous solution is treated with acetic anhydride, acetic peroxide is regenerated owing to the action of the acetic anhydride on the per-acid. When a similar solution is treated with benzoyl chloride, a mixture of benzoic and benzoic acetic peroxides is produced.

The authors were unable to isolate peracetic acid. Its aqueous solution slowly bleaches indigo, but more rapidly in presence of dilute sulphuric acid. It liberates chlorine from hydrochloric acid. If a drop of potassium permanganate solution is added to a solution slightly acidified with sulphuric acid, it is not affected, but in a strongly acid solution it is soon decolorised owing to hydrolysis of the peracetic acid with formation of hydrogen peroxide. It does not oxidise alcohol. When silver oxide or lead monoxide is added to the solution, a rapid evolution of oxygen occurs, whilst manganese dioxide is oxidised to permanganic acid.

Propionic peroxide, prepared in the same manner as acetic peroxide, is soluble in water to the extent of 15·9 grams per litre, and is miscible with all the ordinary solvents. When heated at 80°, it slowly decomposes with evolution of hydrocarbons and carbon dioxide and formation of a gummy residue. It does not solidify at −20°. The aqueous solution slowly undergoes hydrolysis with formation of perpropionic acid; the velocity of the change at 20° was determined. *Perpropionic acid* closely resembles peracetic acid in its chemical behaviour.

Crotonic anhydride, obtained by the action of acetic anhydride on crotonic acid, boils and decomposes slightly at 128—130° under 19 mm. pressure, has a sp. gr. 1·0338 at 29°/29°, and does not solidify at −15°. The *peroxide* crystallises in needles and irregular plates, melts at 41°, is odourless, explodes gently on heating, and is soluble in all the usual solvents. In aqueous solution, it slowly suffers hydrolysis with formation of percrotonic acid. A hydrolysed solution was extracted with light petroleum to remove unaltered peroxide, and afterwards with ether; on evaporating the ethereal solution, a crystalline residue was obtained which had the characteristic per-acid odour.

Benzoic acetic peroxide undergoes hydrolysis in aqueous solution with production of perbenzoic and acetic acids, together with benzoic peroxide. In aqueous solution, perbenzoic acid is slowly converted into benzoic acid and hydrogen peroxide; the rate of the change was determined. Perphthalic acid is hydrolysed with greater rapidity, the change in this case being complete in 4 days. E. G.

Structure of Hydroxystearic Acids. Al. A. Shukoff and P. I. Schestakoff (*J. Russ. Phys. Chem. Soc*, 1903, 35, 1—22).—The authors have determined the structure of the following hydroxystearic acids.

ι-Hydroxystearic acid, $CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot[CH_2]_8\cdot CO_2H$. This

acid, which was formerly known as β-hydroxystearic acid and melts at 83—85°, is the one obtained from sulpho- or iodo-derivatives of oleic acid, and is best prepared by the action of sulphuric acid on oleic acid. When oxidised by means of chromic acid in glacial acetic acid solution, it yields sebacic and azelaic acids, traces of suberic acid and of liquid monobasic acids, and ketostearic acid identical with that obtained by Baruch from stearolic acid (Abstr., 1894, i, 170).

κ-Hydroxystearic acid, $CH_3\cdot[CH_2]_6\cdot CH(OH)\cdot[CH_2]_9\cdot CO_2H$, melting at 84—85° and known previously as α-hydroxystearic acid, is obtained from *iso*oleic acid by the action of stearic acid. When oxidised in glacial acetic acid by means of chromic acid, it yields: (1) sebacic acid; (2) *nonylene-$\alpha\iota$-dicarboxylic acid*, $CO_2H\cdot[CH_2]_9\cdot CO_2H$, which is slightly soluble in water and, after crystallisation from benzene and chloroform, melts at 124°; (3) *κ-ketostearic acid*, $CH_3\cdot[CH_2]_6\cdot CO\cdot[CH_2]_9\cdot CO_2H$, which crystallises from alcohol and acetic acid in large plates melting at 65° and is readily soluble in ether; the *calcium* salt was prepared and analysed. This keto-acid is also obtained from *iso*oleic acid by converting it into the corresponding dibromostearic acid, transforming this, by means of alcoholic potassium hydroxide, into *iso*stearolic acid, and treating the latter with concentrated sulphuric acid. From the results obtained, the authors conclude that *iso*oleic acid has the constitution $CH_3\cdot[CH_2]_6\cdot CH\dot{:}CH\cdot[CH_2]_8\cdot CO_2H$.

γ-Hydroxystearic acid exists only in the form of the corresponding lactone, $CH_3\cdot[CH_2]_{13}\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CO\end{matrix}$, which is obtained by heating oleic acid with anhydrous zinc chloride. On oxidation with chromic acid in acetic acid solution, it yields liquid monobasic acids, small quantities of dibasic acids, including succinic acid and *γ-ketostearic acid*, $CH_3\cdot[CH_2]_{13}\cdot CO\cdot[CH_2]_2\cdot CO_2H$, which, after crystallisation from alcohol and acetic acid, forms large, lustrous leaves melting at 97°; the *oxime* of the latter acid is deposited from alcohol in the form of a microcrystalline powder which melts at 85° and is readily soluble in ether. When heated with concentrated sulphuric acid, this oxime is transformed into the *tetradecylamide* of succinic acid,

$$CH_3\cdot[CH_2]_{13}\cdot NH\cdot CO\cdot[CH_2]_2\cdot CO_2H,$$

which crystallises from alcohol in long needles melting at 123° and is readily soluble in acetic acid or ether; treatment of this compound with hydrochloric acid yields succinic acid and tetradecylamine.

T. H. P.

New Derivatives of Cyanoacylacetic Esters. CH. SCHMITT (*Compt. rend.*, 1903, 136, 689—691).—By the action of acid chlorides on the silver salts of cyanoacylacetic esters, substances of an enolic type are obtained. The following substances have been prepared. From acetyl chloride and silver methyl cyanobenzoylacetate, *methyl α-cyano-β-acetoxy-β-phenylacrylate*, $OAc\cdot CPh\dot{:}C(CN)\cdot CO_2Me$, which is very soluble in chloroform, acetone, or alcohol, less so in ether or benzene, and only sparingly so in toluene or light petroleum. It forms monoclinic crystals and melts at 89°. It is easily saponified, giving acetic acid and methyl cyanobenzoylacetate. With an aqueous solu-

tion of potassium hydroxide, it gives cyanoacetophenone and benzoic and acetic acids.

Methyl α-cyano-β-benzoyloxy-β-methylacrylate,

$$OBz\cdot CMe\colon C(CN)\cdot CO_2Me,$$

obtained from benzoyl chloride and silver methyl cyanoacetoacetate, forms slender needles which melt at 61·5°.

Methyl α-cyano-β-benzoyloxy-β-phenylacrylate forms monoclinic plates which melt at 83°; the *ethyl* ester melts at 78—79°.

Methyl α-cyano-β-methoxy-β-phenylacrylate melts at 127—128°; the *ethyl* ester melts at 101·5°.

Methyl α-cyano-β-propyloxy-β-phenylacrylate melts at 84°.

From these, by the action of ammonia, the following amino-compounds have been obtained: *methyl β-amino-α-cyanocinnamate*,

$$NH_2\cdot CPh\colon C(CN)\cdot CO_2Me,$$

which melts at 181—182°, *ethyl β-amino-α-cyanocinnamate*, which melts at 125°, and *methyl β-ethylamino-α-cyanocinnamate*, which melts at 123°. J. McC.

Hydration of Acetylenic Acids. New Method of Synthesis of Unsubstituted β-Ketonic Acids and Esters. Charles Moureu and Raymond Delange (*Compt. rend.*, 1903, **136**, 753—756).—The preparation of β-ketonic acids has been effected by the addition of the elements of water to acetylenic acids in the same manner as the ketones of the type $R\cdot CO\cdot CH_2R'$ have been prepared from acetylene hydrocarbons; this method has, up to the present, only been used by Baeyer in obtaining benzoylacetic acid from phenylpropiolic acid (Abstr., 1883, 336). Owing to the readiness with which the acetylenecarboxylic acids and the β-ketonic acids lose carbon dioxide, the hydration of the former was difficult; it was, however, effected by boiling the acetylenic acid (1 mol.) with 10 per cent. alcoholic potassium hydroxide (3 mols.) for 8 to 10 hours according to the particular case; the alkaline liquor was extracted with ether to remove ketone and acidified with sulphuric acid and then again extracted with ether. The acid was obtained by evaporating the ether under reduced pressure, either as an oil or a crystalline mass; the aqueous solution of the acid always gives a red coloration with dilute ferric chloride. The esters can readily be prepared by saturating an alcoholic solution of the acid with hydrogen chloride or by adding sulphuric acid to this solution, and have been used to characterise the ketonic acids which have been prepared from the acetylenic acids recently described (this vol., i, 312).

Ethyl butyrylacetate, $CH_3\cdot[CH_2]_2\cdot CO\cdot CH_2\cdot CO_2Et$, boils at 94—96° under 15 mm. pressure; its *copper* salt melts at 125—126° (compare Bongert, Abstr., 1902, i, 73; and Blaise, Abstr., 1901, i, 363). Ethyl *iso*butyrylacetate, $COPr^{\beta}\cdot CH_2\cdot CO_2Et$, boils at 76—78° under 10 mm. and at 86—87° under 15 mm. pressure, and has a sp. gr. 1·002 at 0°; its *copper* salt crystallises in white prisms (compare Bouveault, Abstr., 1900, i, 474). Ethyl hexoylacetate was also prepared (compare Bongert, *loc. cit.*; and Bouveault, *loc. cit.*). *Methyl heptoylacetate* boils at 132·5—134° under 19 mm. pressure, and has a sp. gr. 0·982 at 0°; its *copper* salt melts at 98—99°; the *ethyl* ester

boils at 125—127° under 10 mm. and at 132—133° under 13 mm. pressure, and has a sp. gr. 0·9659 at 0°; its *copper* derivative melts at 86°. *Hexylpyrazolone*, $C_6H_{13}\cdot C_3H_3ON_2$, prepared by the action of hydrazine hydrate on these esters, melts at 197°. *Ethyl decoylacetate*,

$$C_9H_{19}\cdot CO\cdot CH_2\cdot CO_2Et,$$

boils at 164—165° under 13 mm. pressure and has a sp. gr. 0·9414 at 0°; its *copper* derivative melts at 108—109°. *Ethyl* iso*heptenoylacetate* [*ethyl η-methyl-Δ^ε-hexenoylacetate*], $CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2Et$, boils at 127—130° under 14 mm. pressure.

The ketones, $R\cdot COMe$, which are always formed in small quantities in the preparation of these β-ketonic acids, become the main product of the reaction when the acetylenic acid is treated with aqueous instead of alcoholic potassium hydroxide. The ketones have been isolated in each case. *Methyl hexyl ketone* yields an *oxime* boiling at 116·5° under 15 mm. pressure and having a sp. gr. 0·8886 at 0°; the *semicarbazone* melts at 121°. Although these acetylenic acids are generally so sensitive to treatment with alkali hydroxides that their esters cannot be hydrolysed, yet trimethyltetrolic acid,

$$CMe_3\cdot C\colon C\cdot CO_2H,$$

is not changed by large excess of hot alcoholic or aqueous potassium hydroxide. K. J. P. O.

β-Hydroxy-β-methyladipic Acid. PAUL DUDEN and R. FREYDAG (*Ber.*, 1903, 36, 953—954).—When finely-divided zinc is added to a mixture of ethyl lævulate and ethyl bromoacetate and the temperature kept at 100—120°, the *ethyl* ester, $\begin{array}{l}CO\text{——}O\\ |\\ CH_2\cdot CH_2\end{array}\!\!>CMe\cdot CH_2\cdot CO_2Et$, of the *lactone* of *β-hydroxy-β-methyladipic acid* is obtained; it boils at 160—162° under 15 mm. and at 285—287° under atmospheric pressure, and dissolves in aqueous alkali hydroxides, giving solutions from which silver nitrate precipitates the gelatinous *silver* salt, $C_9H_{15}O_5Ag$.

W. A. D.

Condensation Product from Diacetyl and Ethyl Oxalate. OTTO DIELS (*Ber.*, 1903, 36, 957—959).—The product of the sodium ethoxide condensation of diacetyl and ethyl oxalate is not tetraketohexamethylene, but *ethyl hexane-αγδζ-tetrone-αζ-dicarboxylate*,

$$CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et,$$

which crystallises from ethyl acetate in yellow leaflets and melts at 126° (corr.). W. A. D.

Methylation and Condensation of Ethyl Glutaconate. EDMOND E. BLAISE (*Compt. rend.*, 1903, 136, 692—694).—By methylating ethyl glutaconate at 0°, ethyl dimethylglutaconate is obtained which boils at 130° under a pressure of 14 mm. On saponification, this ester gives a mixture of the *cis*- and *trans*-forms of αα-dimethylglutaconic acid and αγ-dimethylglutaconic acid.

When ethyl glutaconate (2 mols.) is warmed on the water-bath with alcohol containing sodium (1 mol.), a green, fluorescent solution is obtained and *ethyl glutaconylglutaconate*,

$$CO_2Et\cdot C_3H_4\cdot CO\cdot CH(CO_2Et)\cdot CH\colon CH\cdot CO_2Et,$$

separates; it melts at 77—78°, is soluble in solutions of alkali hydr-

oxides or carbonates, and in alcoholic solution gives a blue coloration with ferric chloride; when titrated in alcoholic solution, it behaves as a monobasic acid. Its *phenylhydrazone* melts at 126—127°. On hydrolysis with acid, a monobasic acid of the formula $C_8H_{12}O_4$ is formed, which easily loses a mol. of water and melts at 66°. Saponification in the cold with alkali gives *diethyl hydrogen glutaconylglutaconate*, which melts at 98—99° and gives a blue coloration with ferric chloride. By careful saponification of ethyl glutaconylglutaconate with alkali at a higher temperature, *ethyl dihydrogen glutaconylglutaconate*, $CO_2H\cdot C_3H_4\cdot CO\cdot CH(CO_2Et)\cdot CH{:}CH\cdot CO_2H$, is obtained, which, when slowly heated, melts at 178°, but when quickly heated, at 218—220°.

During the methylation of ethyl glutaconate, some ethyl glutaconylglutaconate is always formed as well as an oil, which, since it behaves as an α-disubstituted β-ketonic ester, is probably ethyl methylglutaconylglutaconate. J. McC.

Oxidation of Aldehyde-Ammonia. EUGEN BAMBERGER and RICHARD SELIGMAN (*Ber.*, 1903, **36**, 817—818).—It was thought that ammonia might be oxidised by Caro's persulphuric acid to Angeli's nitroxyl, NOH, and that this could be detected by its conversion of acetaldehyde into acethydroxamic acid. The latter was actually formed, but is probably a direct oxidation product of aldehyde-ammonia.

T. M. L.

Oximes of Nitromalonic Aldehyde. HENRY B. HILL and WILLIAM J. HALE (*Amer. Chem. J.*, 1903, **29**, 253—274. Compare Hill and Torrey, Abstr., 1899, i, 788).—When an excess of hydrochloric acid is added to the sodium salt of nitromalonic dialdoxime suspended in water, a bright yellow, crystalline substance is formed which gradually decomposes with formation of β-nitro*iso*oxazole and hydroxylamine. If exactly the calculated quantity of hydrochloric acid is employed in dilute solution, and the β-nitro*iso*oxazole extracted with ether, the deep red aqueous solution is found to contain unaltered dialdoxime, since, on addition of aniline acetate, nitromalonic aldehyde aniloxime is precipitated. When the red solution is made alkaline with sodium hydroxide and then shaken with acetic anhydride, the *sodium* salt of nitromalonic diacetyldialdoxime is produced. If the solution is left for 24 hours, the oxime disappears and a substance, which is isomeric with fulminuric acid and is converted into this acid by boiling it for a few minutes with water, is deposited in slender, colourless needles.

The *disodium* and *disilver* salts of nitromalonic dialdoxime were prepared. The *diacetyl* derivative, $OH\cdot NO{:}C(CH{:}N\cdot OAc)_2$, crystallises in aggregates of colourless needles, melts at 64—66°, and is readily soluble in alcohol or chloroform; its *sodium* salt forms pale yellow needles and melts and decomposes at 136—138°. When this sodium salt is dissolved in warm water, it suffers decomposition with formation of nitromalonic acetylaldoxime nitrile and acetic acid; the same products result from the spontaneous decomposition of the diacetyldialdoxime.

Nitromalonic acetylaldoxime nitrile, CN·C(NO·OH)·CH:N·OAc, crystallises in long prisms, melts at 87—88°, and dissolves readily in alcohol, ether, benzene, or chloroform.

Nitromalonic aldoxime nitrile, CN·C(NO·OH)·CH:N·OH, obtained by heating its acetyl derivative with water at 100°, crystallises in long, colourless, dendritic needles or in irregularly aggregated prisms, melts at 143—144°, and is readily soluble in alcohol, ether, or hot water; its *barium* and *silver* salts are described. If aniline hydrochloride is added to an alkaline solution of the aldoxime nitrile, nitromalonic anil nitrile is formed. When the aldoxime nitrile is heated with excess of potassium hydroxide, fulminuric acid is produced. On addition of hydrochloric acid to a solution of the aldoxime nitrile, the *substance*, $C_3H_3O_3N_3$, identical with the compound formed by the spontaneous decomposition of the dialdoxime in aqueous solution, is slowly deposited. This compound is also produced together with fulminuric acid by the action of hydroxylamine on β-nitro*iso*oxazole. It melts and decomposes at 128° to 140° according to the rate of heating, and is sparingly soluble in cold, but readily so in hot, water; it dissolves in solutions of alkali carbonates with formation of the corresponding salts of fulminuric acid.

The *acetyl* derivative of nitromalonic aldehyde aniloxime crystallises in yellow needles or prisms, melts at 114—116°, and is readily soluble in alcohol, chloroform, benzene, or glacial acetic acid. When heated with Beckmann's mixture, it is converted into *nitromalonic anil nitrile*, CN·C(NO·OH)·CH:NPh, which crystallises in short, yellow prisms, melts at 215—216°, and dissolves readily in hot glacial acetic acid or hot ethyl acetate.

When phenylhydrazine is added to an alcoholic solution of β-nitro*iso*oxazole, 1-phenyl-4-nitropyrazole and hydroxylamine are produced. By the action of phenylhydrazine hydrochloride on an aqueous solution of the sodium salt of nitromalonic dialdoxime, the unstable aldoxime hydrazone is formed as an orange-red, crystalline substance which gradually changes into 4-nitro-1-phenylpyrazole.

An aqueous solution of β-nitro*iso*oxazole rapidly acquires a bright yellow colour and an acid reaction; if aniline or aniline acetate is added to the acid solution, nitromalonic anil nitrile is produced, but if the solution is rendered alkaline with sodium hydroxide before the addition of the aniline salt, nitromalonic aldoxime nitrile is formed. If β-nitro*iso*oxazole is heated with water at 100°, a deep yellow solution is obtained containing formic acid and an acid which yields a bright yellow, crystalline silver *salt*, $C_5HO_4N_4Ag$. E. G.

Theory of the Carbohydrates. William Küster (*Zeit. physiol. Chem.*, 1903, **37**, 221—224).—In addition to the transformation of *d*-glucuronic acid into *l*-xylose (Salkowski and Neuberg, this vol., i, 7), several other similar transformations of *d*- into *l*-compounds are mentioned. J. J. S.

Determination of the Molecular Weight of Nitro-starch. A. V. Saposchnikoff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 126—128).—The author has determined the molecular weight of nitro-starch in boiling acetone, an ordinary Beckmann apparatus being employed.

Two different samples of the nitro-compound were used, one prepared by the method given by Will and Lenze (*Ber.*, 1898, 31, 87; Abstr., 1898, i, 227), and the other by treating starch with a mixture of 1 part of nitric acid of sp. gr. 1·48 and 3 parts of sulphuric acid of sp. gr. 1·84 for 24 hours and then removing the acid and drying. The molecular weights obtained for the two samples were 1824—1842 and 1829—1884 respectively, numbers which agree well with the formula $C_{36}H_{43}(NO_3)_{17}O_{13}$; this formula requires 13·35 per cent. of nitrogen, the numbers actually obtained being 13·44 and 13·43 respectively.

T. H. P.

Hensen's Method of Preparing Glycogen. EDUARD PFLÜGER (*Pflüger's Archiv*, 1903, 95, 17—18).—Hensen's method, published in 1857 (*Virchow's Archiv*, 11, 395), does not seem to have been subsequently tested. The material obtained is impure, but not markedly so.

W. D. H.

Ethylenediamine Compounds of Cadmium. PHILIPPE BARBIER (*Compt. rend.*, 1903, 136, 688—689).—When a moderately concentrated solution of cadmium iodide is added to a concentrated solution of ethylenediamine hydrate, a precipitate is formed which dissolves in excess of the reagent. On spontaneous evaporation of the solution, transparent, prismatic crystals of *tetraethylenediamine cadmium iodide*, $4C_2H_4(NH_2)_2,CdI_2$, separate. When these crystals are moistened, they become opaque. If a solution of this salt is warmed, large, octahedral crystals of *tetraethylenediamine dicadmium iodide*, $4C_2H_4(NH_2)_2,2CdI_2$, separate on cooling. This salt is much more stable than the monocadmium iodide, but is decomposed by prolonged boiling with water. The latter solution yields, on concentration, long, opaque, white needles of *triethylenediamine dicadmium iodide*, $3C_2H_4(NH_2)_2,2CdI_2$, and white, opaque, tetrahedral crystals of tetraethylenediamine dicadmium iodide, which differ from those already mentioned in crystalline form and solubility.

J. McC.

Products of the Action of Nitrous Acid on Tetramethylenylmethylamine. [ω-Aminomethyl*cyclo*butane] NICOLAUS I. DEMJANOFF and M. LUSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 26—42. Compare Abstr., 1901, i, 509).—The authors have continued the investigation of the products described in the preliminary account of their work (*loc. cit.*).

ω-Aminomethyl*cyclo*butane boils at 110° under 753 mm. pressure and not at 82—83° as was stated by Freund and Gudemann (Abstr., 1888, 1271); the authors show that it has the constitution

$$CH_2{<}{}^{CH_2}_{CH_2}{>}CH\cdot CH_2\cdot NH_2.$$

When the hydrochloride of the amine is triturated with silver nitrite and the solution of the nitrite of the amine thus obtained is heated, the principal products consist of:

(i) An alcohol, $C_5H_9\cdot OH$, which boils at 138° under 733 mm. and at 139° under 757 mm. pressure, has the sp. gr. 0·9556 at 0°/0° and 0·9442 at 15°/0°, and n_D 1·452 at 20°. Its acetyl derivative, a liquid with a pleasant, fruity smell, boils at 150—151° under 736 mm. pressure and

has the sp. gr. 0·9866 at 0°/0°, and 0·9722 at 15°/0°, and n_D 1·430 at 17°. On heating the alcohol with fuming hydrobromic acid, it yields mainly bromo*cyclo*pentane together with small quantities of other products containing a larger proportion of bromine. When oxidised by means of chromic and sulphuric acids, the alcohol yields ketopentamethylene and an aldehyde which, on boiling with silver oxide, gives tetramethylenecarboxylic acid. On treating the alcohol with phosphorus and iodine and transforming the iodo-compound thus obtained into the corresponding nitro-compound, the main product is a primary derivative mixed with small quantities of a secondary compound. The authors hence conclude that the alcohol, $C_5H_9 \cdot OH$, consists of a mixture of two compounds having the constitutions:

$$CH_2{<}{\begin{matrix}CH_2\\CH_2\end{matrix}}{>}CH \cdot CH_2 \cdot OH \quad \text{and} \quad \begin{matrix}CH_2 \cdot CH_2\\ | \\ CH_2 \cdot CH_2\end{matrix}{>}CH \cdot OH.$$

(ii) A hydrocarbon, C_5H_8, which boils at 43° under 727 mm. pressure and has the sp. gr. 0·790 at 0°/4° and 0·773 at 18°/4°, and n_D 1·424 at 18°, agreeing with the assumption that one double linking is present in the molecule. With bromine, a dibromo-derivative, $C_5H_8Br_2$, is obtained which boils at 192—193° and has the sp. gr. 1·894 at 0°/0° and 1·869 at 17°/0°, and n_D 1·547 at 17°; when heated with lead oxide in presence of water, the dibromide yields pentamethylene glycol together with small quantities of an aldehyde. The bromide is hence a mixture of dibromo*cyclo*pentane and a dibromide of methyl*cyclo*butane. When treated with sulphuric acid, the hydrocarbon, C_5H_8, gives a mixture of alcohols similar to that described under (i). It is therefore concluded that the hydrocarbon consists of a mixture of *cyclo*pentene,

$$\begin{matrix}CH_2{-}CH\\ | \\ CH_2 \cdot CH_2\end{matrix}{\gg}CH,$$

and methylene*cyclo*butane, $CH_2{<}{\begin{matrix}CH_2\\CH_2\end{matrix}}{>}C{:}CH_2$.

In the action of nitrous acid on ω-aminomethyl*cyclo*butane, there is a partial isomeric transformation of a ring of four carbon atoms into one containing five carbon atoms. T. H. P.

n-Heptyl Thiocyanate and some New Alkyl Esters of Dithiocarbamic Acid. MARSTON T. BOGERT (*J. Amer. Chem. Soc.*, 1903, **25**, 289—291).—n-*Heptyl thiocyanate*, prepared by the action of normal heptyl bromide on potassium thiocyanate, is a colourless oil, boiling at 136° (corr.) under 28 mm. pressure and having the sp. gr. 0·92 at 20°.

n-*Heptanesulphonic acid*, obtained by oxidising the thiocyanate with nitric acid, yields a barium salt crystallising in pearly white scales.

n-*Heptyl dithiocarbamate*, prepared by heating the thiocyanate with hydrogen sulphide under pressure at 100°, forms large, glassy, steatitic prisms melting at 65°.

n-*Propyl dithiocarbamate* was obtained in analogous fashion; it forms monoclinic crystals [$a:b:c = 0·8536:1:0·9447$; $\beta = 77°7'$] melting at 57° (compare Delépine, this vol., i, 236).

iso*Amyl dithiocarbamate*, crystallises in glassy, micaceous scales melting at 51·5°. A. McK.

Reaction between Oximes and Thionyl Chloride and on some Physical Constants of Camphoronitrile. Bronislas Pawlewski (*Bull. Acad. Sci. Cracow*, 1903, 8—9).—Ketoximes are, as a rule, not attacked by thionyl chloride, but camphoroxime and the aldoximes are converted into the corresponding nitriles; thus, benzaldoxime furnishes benzonitrile and a small quantity of a solid substance which melts at 224°. Camphoronitrile, prepared by this method, boils at 228·2° under 760 mm. pressure and has the sp. gr. 0·9227 at 0°, 0·9113 at 20°, and 0·9098 at 40°. The specific heat between 0° and 40° is 0·476, the specific refraction $(n-1)/d$ 0·5158 and $[\alpha]_D$ +4·02° at 20°.

T. A. H.

Action of Phosphorus Trichloride on Ethylene Glycol. P. Carré (*Compt. rend.*, 1903, 136, 756—758).—Phosphorus trichloride reacts very vigorously with ethylene glycol, 1—2 mols. of hydrogen chloride being set free. When the two reagents are diluted with ether, two substances can be isolated, one soluble in ether and the other insoluble. The former, which represents 75 per cent. of the product of the reaction, is an unstable *substance*, the analyses and mol. weight determination (in benzene) of which lead to the formula $P_2Cl_2(O_2{:}C_2H_4)_2$. When decomposed by water, it yields a solution containing the *acid*, $P_2(O_2{:}C_2H_4)_2(OH)_2$, which behaves as a dibasic acid towards methyl-orange and phenolphthalein; its *calcium* salt, $P_2(O_2{:}C_2H_4)_2O_2Ca$, was prepared. But when the temperature used in decomposing the chloride with water was high, another *acid*, $P_2(O_2{:}C_2H_4)(OH)_4$, was obtained, glycol being eliminated; this acid was also dibasic towards methyl-orange and phenolphthalein, and yielded a semicrystalline *calcium* salt, $P_2(O_2{:}C_2H_4)(OH)_2O_2Ca$. Boiling water completely hydrolyses both these acid esters.

The *substance*, which is insoluble in ether, $OH{\cdot}PCl{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$, is converted by boiling with water into phosphorous acid and glycol chlorohydrin; when hydrolysed by cold water, a solution of the acid, $P(OH)_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$, which is monobasic towards methyl-orange and phenolphthalein is obtained; its *barium* salt,

$$[OH{\cdot}P(O{\cdot}CH_2{\cdot}CH_2Cl)O]_2Ba,$$

has been prepared. K. J. P. O.

Silicon Compounds. Walther Dilthey (*Ber.*, 1903, 36, 923—930).—*Triacetylacetonylsilicon chloride hydrochloride*, $SiCl(CHAc_2)_3,HCl$, obtained by mixing anhydrous chloroform solutions of acetylacetone (3 mols.) and silicon tetrachloride ($1\frac{1}{4}$ mols.) and subsequently adding ether or light petroleum, crystallises in thick, colourless prisms, melts at 85—89°, and is rapidly decomposed by water into acetylacetone and silicic acid. The *ferrichloride*, $Si(CHAc_2)_3FeCl_4$, prepared by adding anhydrous ferric chloride to a solution of the hydrochloride in chloroform or glacial acetic acid, crystallises in yellow needles with a green lustre and melts and decomposes at 186—187°; bromine converts it into a *substance* crystallising in chocolate-coloured leaflets and melting at 157—158°. The *aurichloride*, $Si(CHAc_2)_3AuCl_4$, crystallises in slender, golden needles melting at 162—163°, and the *platinichloride*, $[Si(CHAc_2)_3]_2PtCl_6$, in thick, reddish-yellow prisms; the *stannochloride*

forms thick, white needles, whilst two *stannichlorides* are described, one crystallising in white needles melting at 214—216° and the other in nacreous leaflets melting at 140°.

Acetylacetone (3 mols.) interacts with stannic chloride (2 mols.) in cold chloroform solution giving a *substance* having the composition $SnCl_2(CHAc_2)_2$, which is probably *triacetylacetonyltin stannichloride*, $[Sn(CHAc_2)_3]_2SnCl_6$; it crystallises from hot alcohol in white prisms and melts and decomposes at 202°. W. A. D.

Colloidal Copper Acetylide. FRANZ KÜSPERT (*Zeit. anorg. Chem.*, 1903, **34**, 453—454).—If an ammoniacal solution of cuprous chloride is added to an aqueous solution of acetylene, a red pseudo-solution of copper acetylide is formed. This solution cannot be filtered, but if 0·2 per cent. of gelatin is added, a stable colloidal solution is obtained. J. McC.

Action of Auxochromic Groups. HUGO KAUFFMANN (*Zeit. Farb. Text. Chem.*, 1903, **2**, 109—110).—A theoretical paper unsuitable for abstraction (compare Kauffmann and Beisswenger, this vol., i, 330). W. A. D.

Action of Dipropylamine on the Isomeric Nitrohalogen-benzenes. ELMARA PERNA (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 114—119. Compare Nagornoff, Abstr., 1899, i, 425).—Dipropylamine (2 mols.) reacts with the nitrohalogen-benzenes yielding the halogen hydracid salts of dipropylamine and nitrodipropylaniline, the velocity of the reaction depending on the nature of the halogen present and its position relatively to the nitro-group (see Nagornoff, *loc. cit.*). The author has studied this reaction when the different chloro-, bromo-, and iodo-nitrobenzenes are employed. The following tables give the percentages of the halogen compounds attacked when heated with two molecular proportions of dipropylamine at 130° and at 183°:

	At 130°.			At 183°.		
	Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
$C_6H_4Cl(NO_2)$	13·06	0	0·83	76·7	0	3·6
$C_6H_4Br(NO_2)$	19·86	0	1·44	88·6	0	21·3
$C_6H_4I(NO_2)$	32·05	0	1·17	decomposed	1·2	15·0

T. H. P.

Certain Derivatives of Picric Acid. C. LORING JACKSON and R. B. EARLE (*Amer. Chem. J.*, 1903, **29**, 212—215).—*Picryl bromide* (1-*bromo*-2 : 4 : 6-*trinitrobenzene*), $C_6H_2Br(NO_2)_3$, obtained by the nitration of 1-bromo-2 : 4-dinitrobenzene, crystallises from alcohol in long, yellowish-white plates, melts at 122—123°, and is freely soluble in

benzene or acetone; by the action of sodium methoxide, it is converted into trinitroanisole.

Phenyl picrate, first prepared by Willgerodt (Abstr., 1879, 923), crystallises from a mixture of alcohol and benzene in short, thick, yellow prisms, melts at 153°, and dissolves readily in benzene, acetone, or hot glacial acetic acid. It reacts with ethyl sodioacetoacetate with formation of ethyl trinitrophenylacetoacetate described by Dittrich (Abstr., 1890, 1418).

4-*Bromo-2-nitrophenyl picrate*, $C_6H_2(NO_2)_3 \cdot O \cdot C_6H_3Br \cdot NO_2$, obtained by the action of picryl chloride on sodium 4-bromo-2-nitrophenoxide, crystallises in short, thick, yellowish-white prisms, melts at 232°, is soluble in acetone or hot benzene, and turns brown on exposure to the air; it reacts with ethyl sodioacetoacetate, but the product has not been investigated. E. G.

3 : 5-Dinitrobenzenesulphonic Acid. C. Loring Jackson and R. B. Earle (*Amer. Chem. J.*, 1903, **29**, 216—225).—3 : 5-Dinitrobenzenesulphonic acid, prepared from 1 : 3 : 5-dinitroaniline by decomposing the diazoethylxanthate and oxidising the product, was found to be identical with the acid first obtained by Limpricht (this Journal, 1876, ii, 303) by the nitration of *m*-nitrobenzenesulphonic acid, and afterwards studied by Sachse (Abstr., 1877, ii, 751), who assigned to it the constitution [$NO_2 : NO_2 : SO_3H = 2 : 3 : 1$]. The sulphochloride crystallises in yellowish-white prisms and melts at 98—99°. The sulphonamide forms short, slender, yellow prisms and melts at 234—235°. The *barium* salt crystallises with $3H_2O$. 3 : 5-Dibromobenzenesulphonic acid, obtained from the dinitrobenzenesulphonic acid by the method employed by Sachse, was converted into the amide which melts at 203°, and is soluble to the extent of 0·006 gram in 100 grams of water at 18° (compare Lenz, Abstr., 1876, ii, 199). E. G.

The Esters of *p*-Toluenesulphonic Acid as Alkylating Agents. Fritz Ullmann and P. Wenner (*Annalen*, 1903, **327**, 120—124. Compare this vol., i, 394).—Both methyl and ethyl *p*-toluenesulphonates are excellent alkylating agents, but the difficulties which attend their preparation will limit their use, especially that of the methyl ester. Both esters are prepared by treating the sulphonic chlorides with the corresponding alcohol (1·5—2 mols.). The naphthols were alkylated by shaking their alkaline solutions with the sulphonic ester, and gave in both cases nearly theoretical yields of the corresponding ethers. When phenylacridine is heated with methyl *p*-toluenesulphonate in nitrobenzene solution, *methylphenylacridinium* p-*toluenesulphonate* is obtained as greenish-yellow leaflets. From 3-acetamino-2-methyl-1 : 2-naphthacridine, 3-*acetylamino*-2-*methyl*-10-*ethyl*-1 : 2-*naphthacridinium* p-*toluenesulphonate* was prepared in a similar manner; it crystallises in yellow leaflets. From 2-methyl-3-amino-3-dimethylaminophenazine (toluylene-red), *methyltrimethyldiaminophenazonium nitrate* was obtained in dark green leaflets, dissolving in alcohol with a red coloration and a reddish-violet fluorescence; its solution in sulphuric acid is bluish-green, which becomes first blue and then reddish-violet on addition of water. In the same manner the corresponding *ethyl*

nitrate was prepared, and resembled very closely the substance just described. K. J. P. O.

Constitution of Derivatives of Acenaphthene and of Naphthalic Acid. Carl Graebe (*Annalen*, 1903, **327**, 77—103).—The nitro-, amino-, acetyl, and benzoyl derivatives of acenaphthene have been prepared, and the substituting group has been shown to be in the 4-position in the naphthalene ring relatively to the methylene group, as they all can be converted into α-naphthylamine.

[With N. Briones.]—4-Nitroacenaphthene is best prepared by adding nitric acid, free from nitrous acid, to a solution of acenaphthene in acetic acid, and melts at 106°; Quincke (Abstr., 1888, 843) records the melting point 101—102°. The nitro-derivative is best reduced to the corresponding amino-derivative by a warm solution of stannous chloride; the base melts at 108°, and its acetyl derivative at 186° (compare Quincke, *loc. cit.*, who records the melting point as 175°). Oxidation of 4-nitroacenaphthene by means of chromic acid in acetic acid solution is recommended as the best method of preparing 4-nitronaphthalic acid; the *ethyl* ester of the latter, prepared only from the silver salt, melts at 86°, and the *imide*, prepared by repeated evaporation of the solution of the acid with ammonia, at 284°. 4-Aminonaphthalic acid is obtained by reducing 4-nitrophthalic acid with stannous chloride in alcoholic solution, and melts at 200°; when its sodium salt is heated with calcium hydroxide, it is converted into α-naphthylamine. 3-Nitronaphthalic acid, prepared by nitrating naphthalic acid by a mixture of nitric and sulphuric acids, melts at 247°, and on reduction with stannous chloride yields 3-aminonaphthalic acid, from which β-naphthylamine can be prepared.

[With M. Guinsbourg.]—4-Bromoacenaphthene (Blumenthal, *Ber.*, 1874, 7, 1095) is best prepared by brominating acenaphthene in solution in boiling chloroform; it melts at 52° and boils at 335°; its *picrate* crystallises in yellow needles melting at 137°. It is best oxidised to 4-bromonaphthalic acid by sodium dichromate in acetic acid solution; the latter can easily be converted into 1-bromonaphthalene. By melting with potassium hydroxide at 290—300°, the acid is converted into 4-hydroxynaphthalic acid, the anhydride of which melts at 257°. When oxidised at 100° in acetic acid solution with sodium dichromate, bromoacenaphthene is converted into 4-*bromoacenaphthaquinone*, which crystallises in yellow needles melting at 194°; the *dioxime* was prepared; the *monophenylhydrazone* crystallises in reddish-brown needles melting at 153°, and the *diphenylhydrazone* in brown needles melting at 134°. When heated with concentrated ammonia at 100°, the quinone does not lose bromine, but becomes converted into the *compound*, $\left(\begin{matrix}C_{10}H_5Br\cdot C\cdot \\ | \qquad\quad | \\ C\!=\!=\!=\!=\!N\end{matrix}\right)_2O$, which is a red powder and does not melt at 300°. On heating the quinone with very concentrated potassium hydroxide at 150°, bromine is replaced by hydroxyl, and a *hydroxynaphthaldehydic acid*, $CHO\cdot C_{10}H_5(OH)\cdot CO_2H$, is formed, melting at 100° and yielding, under the action of acetic anhydride, a *diacetyl* derivative, $OAc\cdot C_{10}H_5{<}\begin{matrix}CH(OAc)\\CO\text{———}\end{matrix}{>}O$, which crystallises in needles melt-

ing at 183°. The *phenylhydrazone* crystallises in yellow needles melting at 219°. *Bromophenylglyoxyldicarboxylic acid*,

$$CH{<}^{CBr\cdot C(CO_2H)}_{CH:C(CO_2H)}{>}C\cdot CO\cdot CO_2H,$$

is obtained by oxidising bromonaphthalic acid by potassium permanganate in alkaline solution, and forms crystals soluble in water and melting at 192°.

[With PAUL HAAS.]—4-*Acetylacenaphthene*, $OAc\cdot C_{10}H_5{<}^{CH_2}_{CH_2}$, is prepared by treating acenaphthene (1 mol.) with acetyl chloride (1 mol.) in carbon disulphide solution and then adding aluminium chloride; the acetyl derivative is finally purified by distillation, when it boils at 361°; it forms colourless crystals melting at 75°; the *picrate* crystallises in orange-red needles melting at 95°; the *oxime* crystallises in plates melting at 165°. When the latter is heated in acetic acid solution containing acetic anhydride and saturated with hydrogen chloride at 100° under pressure, it is converted into 4-acetylaminoacenaphthene. On oxidising acetylacenaphthene with sodium dichromate in acetic acid solution, *acetylnaphthalic anhydride*, $OAc\cdot C_{10}H_5{<}^{CO}_{CO}{>}O$, is formed, and is obtained as crystals melting at 189°; when oxidised with permanganate, it is converted into 1 : 4 : 8-*naphthalenetricarboxylic acid*, the anhydride of which melts at 243°; the *silver* salt was prepared.

4-*Benzoylacenaphthene* was prepared in the same manner as the acetyl derivative; it forms white crystals, melts at 101°, and can be distilled; the *phenylhydrazone* crystallises in long needles melting at 140°, and the *oxime* in needles melting at 185°. The latter undergoes the Beckmann transformation, yielding first a benzoyl derivative melting at 199°, which on hydrolysis is converted into 4-aminoacenaphthene. 4-*Benzoylnaphthalic acid*, prepared by oxidising benzoylacenaphthene with sodium dichromate in acetic acid solution, changes on heating into its *anhydride*, which melts at 195°; the *oxime* of the acid melts at 199°. When the calcium salt is distilled, benzoylnaphthalene (m. p. 73—75°) is formed; this was converted into its oxime and then into benzoylnaphthalide, which, on hydrolysis, gave α-naphthylamine.

[With C. PERUTZ.]—4-*Acenaphthoyl*-o-*benzoic acid*,

$$^{CH_2}_{CH_2}{>}C_{10}H_5\cdot CO\cdot C_6H_4\cdot CO_2H,$$

is prepared by treating a mixture of acenaphthene and phthalic anhydride, dissolved in carbon disulphide, with aluminium chloride, and forms crystals melting at 200°; the *methyl* ester melts at 128° and yields a *picrate* of reddish-yellow colour melting at 135°; the *ethyl* ester melts at 111° and its *picrate* at 126°. On oxidising the acid with sodium dichromate and acetic acid, 4-*benzoylnaphthalene*-1 : 8 : 2′-*tricarboxylic acid*, $C_{10}H_5(CO_2H)_2\cdot CO\cdot C_6H_4\cdot CO_2H$, is formed, and can be isolated in the form of its *anhydride*, which melts at 229°; when evaporated several times with ammonia, it is converted into an *imide*,

$$NH{<}^{CO}_{CO}{>}C_{10}H_5\cdot CO\cdot C_6H_4\cdot CO_2H,$$

melting above 300°. [With PAUL HAAS.]—When the calcium salt of

acenaphthoylbenzoic acid is distilled, 4-benzoylacenaphthene is obtained. This acid can only be converted into *acenaphthanthraquinone*,

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C_{10}H_4<\!\!\begin{matrix}CO\\CO\end{matrix}\!\!>C_6H_4,$$

by heating it with phosphoric chloride at 200°; the quinone forms greenish-yellow crystals melting at 215—220°. K. J. P. O.

Action of Molten Potassium Hydroxide on Fluorene. Synthesis of *o*-Phenylbenzoic Acid. MAX WEGER and K. DÖRING (*Ber.*, 1903, 36, 878—881).—On converting a specimen of fluorene (which was free from oxygen, melted at 113·5—114·5°, and 90 per cent. of which boiled between 287° and 298°) into the potassium derivative by heating at 295—300° with molten potassium hydroxide, the method now in general use for purifying fluorene, it was found that the small quantity of phenanthrene in the crude fluorene partially passed over into the solution of the fluorene in the potassium hydroxide. In order to avoid the presence of phenanthrene, the fraction from which the fluorene is to be isolated must be chosen of somewhat lower boiling point; the acenaphthene, which is now present in small amount, is volatilised during the heating with potassium hydroxide. During the heating with molten potassium hydroxide, *o*-phenylbenzoic acid (m. p. 113·5—114·5°) is always produced, the amount increasing with the duration of heating. It is probably formed from fluorene according to the equation: $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CH_2 + KOH + H_2O =$ $C_6H_4Ph\cdot CO_2K + 2H_2$; the evolution of hydrogen was experimentally demonstrated. K. J. P. O.

Derivatives of Bromoacetoanilide. KURT SCHEDA (*Arch. Pharm.*, 1903, 241, 122—127).—Compounds of the type $NR'''X\cdot CH_2\cdot CO\cdot NHPh$ [$R''' = Me_3$, C_5H_5, or C_9H_7; X = Br or Cl] were prepared. The bromo-compounds were obtained by digesting trimethylamine, pyridine, quinoline, or *iso*quinoline respectively with bromoacetoanilide, in the first case in alcoholic solution; by treating these with silver chloride, the chloro-compounds were prepared. *Acetoanilide-trimethyl-, -pyridine-, -quinoline-,* and -iso*quinoline-ammonium bromides* melt at 201—203°, 199—200°, 225—227°, and 216—218° respectively; the third crystallises with $1H_2O$. The *chlorides* (the trimethylamine and quinoline derivatives crystallise with $1H_2O$) melt (or decompose) at 204—207°, 234°, 210—212°, and 202—206° respectively; the *aurichlorides* at 170—171°, 180—181°, 180—185°, and 167—175°; the *platinichlorides* at 214—228°, 204—206°, 224—236°, and 220—?°; the *mercurichlorides* (with $1HgCl_2$) at 192—197°, 187—189°? (could not be obtained constant in composition), and 198—200°. Some of the trimethylamine and pyridine derivatives had been prepared by another method (compare this vol., i, 427). C. F. B.

***o*-Aminobenzenesulphonamide and its Derivatives and Diazosulphonine Compounds.** ALFRED EKBOM (*Bihang K. Svenska Vet.-Akad. Handl.*, 1902, 27, ii, [i], 3—24).—*o-Aminobenzene-*

sulphonamide, $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, prepared by reducing the corresponding nitroamide by means of red phosphorus and hydriodic acid, crystallises from water in prisms which melt at 152·5—153·5°, and are readily soluble in alcohol; its *hydrochloride* separates in colourless needles. The *monoacetyl* derivative, $NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, is deposited from alcohol in large, many-faced, monoclinic crystals [$a : b : c = 0{\cdot}8570 : 1 : 0{\cdot}7128$; $\beta = 102°40'$] melting at 145—148°. The *diacetyl* derivative crystallises from alcohol in long, transparent prisms melting at 191·5—192·5°. The *monomethyl* derivative,

$$NHMe{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2,$$

is deposited from aqueous solution in slender needles melting at 114·5—115·5°. The *dimethyl* compound crystallises from water in monoclinic plates [$a : b : c = 2{\cdot}0332 : 1 : 1{\cdot}3893$; $\beta = 96°28'$] melting at 105·5—106·5°. The *acetylmethyl* derivative, $NMeAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, crystallises from alcohol in colourless prisms which sinter at 160° and melt at 174—177°. The *carbamide*-derivative,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

crystallises from water in colourless needles melting at 152·5—153·5°.

2-*Methyl*iso*pheno*-1 : 3 : 4-*diazosulphonine*, $C_6H_4{<}\begin{matrix}SO_2{\cdot}N\\ \quad\;\; \| \\ NH{\cdot}CMe\end{matrix}$, obtained, together with water, when monoacetylaminobenzenesulphonamide is heated above its melting point, separates from alcohol in colourless, triclinic prisms [$\alpha = 115°57'$, $\beta = 139°51'$, and $\gamma = 117°41'$] melting at 263—264°. The *methyl* derivative, 1 : 2 *dimethyl*iso*pheno*-1 : 3 : 4-*diazosulphonine*, $C_9H_{10}O_2N_2S$, crystallises from alcohol in slender needles melting at 237—238°.

iso*Pheno*-1 : 3 : 4-*diazosulphonine*, $C_6H_4{<}\begin{matrix}SO_2{-}N\\ \quad\;\; \| \\ NH{\cdot}CH\end{matrix}$, obtained by condensing *o*-aminobenzenesulphonamide by means of formic acid, crystallises from water in colourless, monoclinic prisms [$a : b : c = 2{\cdot}2685 : 1 : 5{\cdot}3846$; $\beta = 91°44'$] melting at 219—220°. T. H. P.

Schiff's Additive Products from Ethyl Acetoacetate and Benzylideneaniline. FRANCIS E. FRANCIS (*Ber.*, 1903, 36, 937—941. Compare Schiff, this vol., i, 172; Biltz, i, 172; Rabe, i, 62).—The author could only obtain, under the conditions originally described by Schiff, two of the three forms of ethyl benzylideneanilineacetoacetate; when pure, they melt at 107—108° (Schiff gives 103—104°) and at 80° (Schiff gives 78°). The supposed keto-enolic mixed form melting at 95° is only an easily separable mixture of these two modifications.

The modification melting at 80°, when heated for 2 hours at 100° and subsequently recrystallised from a mixture of benzene and light petroleum, is converted largely into the form melting at 107—108°; that the latter is the more stable form is shown by its largely remaining unchanged when heated for 45 minutes at 80°.

In determining the mol. weight of the two modifications by the cryoscopic method, much lower values were always obtained than that corresponding with the formula $C_{19}H_{21}O_3N$; the author thus supports Rabe and Biltz in their opposition to Schiff. W. A. D.

Additive Products from Benzylideneaniline and Methyl Acetoacetate. M. TAYLOR (*Ber.*, 1903, 36, 941—944. Compare preceding abstract).—By the interaction of benzylideneaniline with methyl acetoacetate (1 or 2 mols.), a *methyl benzylideneanilineacetoacetate*, $C_{18}H_{19}O_3N$, is obtained, which, after being thoroughly washed with benzene or ether, melts at 125°.

A more soluble *isomeride*, melting at about 86°, is obtained when the action is carried out in presence of piperidine or when the substance melting at 125° is recrystallised from a mixture of benzene and light petroleum containing piperidine. Determinations of the molecular weight by the cryoscopic and ebullioscopic methods show that both forms are unimolecular and that they are gradually decomposed by the solvent. That the two modifications are dynamic isomerides is shown by the melting point of each gradually changing; after several months, the melting point of one form fell from 125° to 113°, whilst that of the other rose from 87° to 98°. W. A. D.

A New Method of Separating Racemic Compounds into Optically Active Components. EMIL ERLENMEYER, jun. (*Ber.*, 1903, 36, 976—978).—The method is based on the fact that many amino-compounds combine with carbonyl compounds to form substances containing the group ·N:C:, which are hydrolysed by mineral acids.

iso-α-Hydroxy-αβ-diphenylethylamine, which has already been shown (Abstr., 1898, i, 480; 1899, i, 760) to combine with aldehydes, was condensed with helicin in alcoholic solution. A crop of dextrorotatory crystals, melting at 189°, was obtained after a time, whilst the solution, when evaporated to dryness, gave an amorphous, lævorotatory substance melting between 80° and 90°; on hydrolysis with hydrochloric acid, these substances yielded the corresponding amino-bases, which agreed in physical constants with the amine as originally resolved by tartaric acid (Abstr., 1899, i, 882). E. F. A.

The Pentene Ring. E. B. AUERBACH (*Ber.*, 1903, 36, 933—936). —When deoxybenzoinbenzylideneacetophenone,

$$COPh\cdot CH_2\cdot CHPh\cdot CHPh\cdot COPh,$$

is reduced with zinc dust in boiling glacial acetic acid solution, it gives the *pinacone*, $CHPh<\begin{matrix}CH_2\text{---}CPh\cdot OH\\ CHPh\cdot CPh\cdot OH\end{matrix}$, which crystallises from a mixture of alcohol and light petroleum in large plates or pyramids, melts at 171°, and is converted by boiling alcoholic hydrochloric acid into the *tetraphenyl*cyclo*pentadiene* or *tetraphenylpentene*,

$$CHPh<\begin{matrix}CH{=}CPh\\ CPh{:}CPh\end{matrix}.$$

This melts at 177—178° and is identical with the substance,

$$CH_2<\begin{matrix}CPh{:}CPh\\ CPh{:}CPh\end{matrix},$$

obtained by Wislicenus and Carpenter (Abstr., 1899, i, 60) from 1 : 3-dibenzoyl-1 : 3-diphenylpropane, and the identity here is probably due to a similar cause to that whereby only one penta-substitution derivative of benzene exists in the case where the five radicles are

identical. The pentene ring is thus analogous to the benzene nucleus. W. A. D.

p-Methoxyphenylacetylene and its Derivatives. FRANZ KUNCKELL and K. ERAS (*Ber.*, 1903, 36, 915—916. Compare Abstr., 1901, i, 75).—p-*Methoxyphenylacetylene*, $OMe\cdot C_6H_4\cdot C\vdots CH$, can be obtained by heating $\alpha:\beta$-dichloro-*p*-methoxystyrene with anhydrous ether and metallic sodium for three days at 90° in sealed tubes, and decomposing with water the sodio-derivative so obtained. It is a colourless oil distilling at 85—88° under 11 mm. pressure, and has a sp. gr. 1·008 at 17°. It has a pleasant odour, dissolves in most organic solvents, and forms metallic derivatives.

p-*Methoxyphenylchloroacetylene*, $OMe\cdot C_6H_4\cdot C\vdots C\cdot Cl$, obtained by the action of alcoholic potash on the dichlorostyrene at 180°, is a pale yellow oil distilling at 133—138° under 20 mm. pressure, and having a sp. gr. 1·180 at 17°. J. J. S.

Constitution of Mononitroso-orcinol. FERDINAND HENRICH (*Ber.*, 1903, 36, 882—885. Compare Abstr., 1902, i, 447).—Orcinol (3 : 5-dihydroxytoluene) is converted by nitrous acid in alkaline solution into two (α and β) mononitroso-orcinols, both of which exhibit strong acid properties, giving, when treated with methyl alcoholic hydrogen chloride, one and the same monomethyl ether; the latter is readily reduced to amino-3-hydroxy-5-methoxytoluene, the position of the amino-group being uncertain. The constitutions of the mononitroso-orcinol and the amino-compound have been determined by nitrating orcinol monomethyl ether (5-hydroxy-3-methoxytoluene), when two mononitro-derivatives are obtained. Both these compounds can be reduced to the same amino-orcinol, the methoxy-group being at the same time replaced by hydroxyl. Consequently the amino-orcinol must be 2-amino-3 : 5-dihydroxytoluene, and the two nitro-compounds must be respectively 2-nitro-3-methoxy-5-hydroxytoluene and 6-nitro-3-methoxy-5-hydroxytoluene. Further, the amino-orcinol is identical with that prepared by the reduction of α- and β-mononitroso-orcinols, and therefore these substances must both be 2-nitroso-3 : 5-dihydroxytoluenes. K. J. P. O.

Two Mononitro-derivatives of Orcinol. FERDINAND HENRICH and W. MEYER (*Ber.*, 1903, 36, 885—889. Compare preceding abstract).—On nitrating orcinol, Weselsky (Abstr., 1874, 694) obtained two mononitro-derivatives, one of which, the α-compound, was volatile with steam, whilst the other, the β-compound, was not volatile. These two nitro-derivatives have now been obtained in much larger quantity by the action of nitric acid of sp. gr. 1·515 on a very dilute solution of orcinol in ether; the α-compound, which forms by far the smaller proportion of the product, is separated from the β-compound by distillation with steam. The α-nitro-compound crystallises in long, orange needles melting at 127° (Weselsky, *loc. cit.*, gives 120°); it is a weak acid and is not converted into its monomethyl derivative by methyl alcohol and hydrogen chloride. The β-nitro-derivative melts at 122° (Weselsky gives 115°), and cannot be esterified by methyl

alcohol; the *potassium* salt, $NO_2 \cdot C_6H_2Me(OH) \cdot OK$, forms green crystals; the *silver* salt is a pale orange-yellow powder. On reduction, the β-nitro-derivative yields 2-amino-3:5-dihydroxytoluene (β-amino-orcinol), and is therefore 2-nitro-3:5-dihydroxytoluene; the α-nitro-derivative must be the only other mononitro-orcinol, 4-nitro-3:5-dihydroxytoluene.

2-*Amino*-3:5-*dihydroxytoluene*, $NH_2 \cdot C_6H_2Me(OH)_2$, prepared from the corresponding nitro-derivative by reduction with stannous chloride, forms a *hydrochloride* which crystallises in rhombohedral forms with $2H_2O$ and is sparingly soluble in dilute hydrochloric acid; with ferric chloride, it gives immediately a dark brownish-red cloud, which rapidly gives place to a pale brownish-yellow coloration; sodium hydroxide gives rise to a brownish-yellow opalescence, which quickly becomes darker as oxidation proceeds; potassium dichromate colours the solution garnet-red.

4-*Amino*-3:5-*dihydroxytoluene*, prepared from the corresponding nitro-derivative (α-nitro-orcinol), yields a *hydrochloride* which crystallises in long, white, anhydrous needles easily soluble in dilute hydrochloric acid; with ferric chloride, the solution becomes at first pale yellow and then pale brownish-yellow; in the presence of sodium hydroxide, oxidation takes place with the formation of a green solution, which finally becomes a dark brownish-yellow; potassium dichromate develops first a greenish-yellow and then a brownish-yellow coloration.

K. J. P. O.

Action of Nitric Acid on the Monomethyl Ether of Orcinol. FERDINAND HENRICH and G. NACHTIGALL (*Ber.*, 1903, **36**, 889—895. Compare preceding abstracts).—Orcinol monomethyl ether is best prepared from orcinol by shaking an alkaline solution of the latter with methyl sulphate and purifying by distillation the product which is extracted by ether from the acidified liquor, when it boils constantly at 256°.

The nitration of the monomethyl ether is effected by slowly adding pure nitric acid to a 3 per cent. solution of the compound in ether, and then separating the volatile α-mononitro-compound from the non-volatile isomeric β-compound by distillation with steam. The α-nitro-derivative, 6-*nitro*-5-*hydroxy*-3-*methoxytoluene*, crystallises in pale yellow needles melting at 104—106°, and has also been prepared by the methylation of β-nitro-orcinol (2-nitro-3:5-dihydroxytoluene). On reduction with stannous chloride, this nitro-ether yields the same base as is obtained from nitroso-orcinol monomethyl ether; the benzoyl derivative melts at 219—220°, and the acetyl derivative at 111—113°; on distillation, the latter gives the usual ortho-condensation product, which sinters at 69° and melts at 71—72° (compare Abstr., 1897, i, 404; 1901, i, 464); when heated with hydrochloric acid, the base loses the methoxyl group and is converted into β-amino-orcinol, 2-amino-3:5-dihydroxytoluene (see previous abstract), the constitution of the base thus being proved.

The non-volatile β-nitro-orcinol, 2-*nitro*-5-*hydroxy*-3-*methoxytoluene*, forms brownish-yellow crystals melting at 129—131°; on reduction with stannous chloride, it is converted into a base, 2-*amino*-5-*hydroxy*-

3-*methoxytoluene*, which closely resembles the isomeride just mentioned; the hydrochloride crystallises in long, flattened needles; when heated with hydrochloric acid, this base is converted into β-amino-orcinol, its constitution thereby being fixed. On oxidation with potassium dichromate, the amino-orcinol monomethyl ether is converted into 3-*methoxytoluquinone*, $CO<\substack{C(OMe){:}CH \\ CMe{=\!=}CH}>CO$, which crystallises in yellow needles melting at 147°. The corresponding *quinol*, prepared by reducing the quinone with sulphurous acid, crystallises in colourless needles melting at 128—129°. K. J. P. O.

Phenol Ethers. I. HERMANN THOMS (*Ber.*, 1903, 36, 854—863). —Hofmann (*Ber.*, 1875, 8, 67) obtained 2 : 3-dimethoxyquinone by the action of nitric acid on 4-hydroxy-2 : 3-dimethoxy-1-propylbenzene; under similar conditions, Will (Abstr., 1888, 458) obtained from 1 : 2 : 3-trimethoxybenzene a nitrotrimethoxybenzene and a dimethoxyquinone. Later, Ciamician and Silber (Abstr., 1890, 1294) investigated the action of nitric acid on asarone (2 : 3 : 5-trimethoxy-1-allylbenzene) and obtained a quinone, methoxypropylquinone, when dihydroasarone was used. The nitration of dihydroasarone has been reinvestigated, and it has been found that when acetic acid is used to dilute the nitric acid the quinone is not formed, but that a nitro-derivative, in which a methoxy-group is replaced by a nitro-group, is produced; this nitro-compound is 4-*nitro*-2 : 5-*dimethoxy*-1-*propylbenzene*, and crystallises in golden-yellow needles melting at 64°; on reduction with aluminium amalgam, 4-*amino*-2 : 5-*dimethoxy*-1-*propylbenzene* is obtained in needles melting at 94°; its *acetyl* derivative crystallises in needles melting at 104°; by elimination of the amino-group from the aminopropylbenzene just mentioned, 2 : 5-*dimethoxy*-1-*propylbenzene* is obtained as an oil boiling at 125° under 20 mm. and at 240° under 760 mm. pressure. The last-mentioned compound was also prepared from 2 : 5-dimethoxybenzaldehyde (dimethylgentisaldehyde), which was converted into 1-*propenyl*-2 : 5-*dimethoxybenzene*, an oil boiling at 132—135° under 14 mm. pressure, by heating with propionic anhydride and sodium propionate under pressure at 175° for 8 hours; on reducing the propenylbenzene with sodium and alcohol, besides 2 : 5-dimethoxy-1-propylbenzene, 2 : 5-*dimethoxy* α-*methylcinnamic acid*, $C_6H_3(OMe)_2{\cdot}CH{:}CMe{\cdot}CO_2H$, melting at 113°, was formed. The dimethoxypropylbenzene, thus synthesised, yielded, on nitration, a a nitro-derivative (m. p. 64°), identical with that obtained by nitrating dihydroasarone.

The quinone (m. p. 111°) obtained by Ciamician and Silber (*loc. cit.*) from dihydroasarone was also prepared; on reduction, it yields a *quinol*, $C_6H_2Pr^{\alpha}(OH)_2{\cdot}OMe$, crystallising in white needles, becoming brown at 75°, and melting at 92°. This quinone was also synthesised from eugenol; the 4 : 5-dimethoxy-1-propenylbenzene was reduced by sodium and alcohol to 4 : 5 *dimethoxy*-1-*propylbenzene*, which is an oily liquid boiling at 246—247°; on nitration in the presence of acetic acid, a *nitro*-derivative, $NO_2{\cdot}C_6H_2Pr^{\alpha}(OMe)_2$, is obtained, and crystallises in pale yellow prisms melting at 81—82°; on reduction, the corresponding *amino*-derivative is formed; it melts at 59° and boils at 169°

under 10 mm. pressure. When a solution of the amino-derivative in dilute sulphuric acid is treated with sodium nitrite, a deep and rapidly changing colour appears; on now warming the solution, the quinone melting at 111° separates in crystals, the amino- and the methoxy-groups having been oxidised away. Ciamician and Silber's quinone is therefore represented by the formula $CO<\begin{matrix}CPr^{\alpha}=CH\\ CH:C(OMe)\end{matrix}>CO$. The nitro-derivative, prepared from 4 : 5-dimethoxy-1-propylbenzene, is, therefore, 2-nitro-4 : 5-dimethoxy-1-propylbenzene; on further nitration with fuming nitric acid at $-20°$, it yields 2 : 6-*dinitro*-4 : 5-*dimethoxy*-1-*propylbenzene*, crystallising in yellow prisms and melting at 66·5°; with sulphuric and nitric acids, 2 : 3 : 6-*trinitro*-4 : 5-*dimethoxy*-1-*propylbenzene* is formed; it crystallises in pale yellow needles melting at 97·3°. K. J. P. O.

Tetraphenylbutanediol and the Products of its Dehydration. AMAND VALEUR (*Compt. rend.*, 1903, **136**, 694—696).—By the action of phenyl magnesium bromide on the esters of dibasic acids, a small quantity of diphenyl is always formed, but this is merely due to a secondary reaction. With methyl oxalate, benzopinacone,

$$OH\cdot CPh_2\cdot CPh_2\cdot OH,$$

is obtained. With ethyl succinate, *tetraphenylbutanediol*,

$$HO\cdot CPh_2\cdot CH_2\cdot CH_2\cdot CPh_2\cdot OH,$$

is formed, which melts at 208° and crystallises from acetone with 1 molecule of that solvent. When heated with acetic acid, it loses 1 mol. of water and gives *tetraphenyltetrahydrofurfuran*, $O<\begin{matrix}CPh_2\cdot CH_2\\ CPh_2\cdot CH_2\end{matrix}$, which melts at 182° and, when warmed with acetic acid containing 10 per cent. of hydrochloric acid or 6 per cent. of sulphuric acid, loses another molecule of water, yielding *tetraphenylbutadiene*,

$$CPh_2:CH\cdot CH:CPh_2;$$

probably a molecule of hydrogen chloride unites the furfuran derivative, so that the compound $HO\cdot CPh_2\cdot CH_2\cdot CH_2\cdot CPh_2Cl$ is formed, which then loses H_2O and HCl. The hydrocarbon crystallises from acetic acid in long needles, melts at 202°, on oxidation gives benzophenone, and on reduction with sodium, tetraphenylbutane. Although unsaturated, the hydrocarbon does not absorb bromine. J. McC.

Pyrogallolsulphonic Acids. MARCEL DELAGE (*Compt. rend.*, 1903, **136**, 760—762. Compare Abstr., 1900, i, 595; 1901, i, 274, 643).—*Strontium pyrogallolsulphonate*, $[C_6H_2(OH)_3\cdot SO_3]_2Sr,2H_2O$, is prepared in the same manner as the calcium and barium salts (*loc. cit.*) and forms small crystals very soluble in water, which rapidly become coloured when left moist in contact with air. *Strontium pyrogalloldisulphonate*, $C_6H(OH)_3(SO_3)_2Sr,3H_2O$, prepared like the corresponding calcium salt, forms crystals which are moderately soluble in water and are less stable than the monosulphonate. In preparing the barium salt of pyrogalloldisulphonic acid (*loc. cit.*), it was observed that a small quantity of an insoluble powder was formed; this compound proves

to be the *salt*, $Ba\left[O\cdot C_6H(OH)_2<^{SO_3}_{SO_3}>Ba\right]_2$; it is converted by acids into the soluble barium salt. K. J. P. O.

Derivatives of *iso*Safrole and *iso*Apiole. F. J. Pond and C. R. Siegfried (*J. Amer. Chem. Soc.*, 1903, 25, 262—272. Compare Pond, Erb, and Ford, Abstr., 1902, i, 449; Auwers and Müller, Abstr., 1902, i, 212).—*β : ?-Dibromo-α-hydroxydihydroisosafrole*,

$$CH_2<^{O}_{O}>C_6H_2Br\cdot CH(OH)\cdot CHMeBr,$$

prepared by boiling bromo*iso*safrole dibromide with aqueous acetone, separates from alcohol in large crystals melting at 89°. The *methoxy*-derivative crystallises in large prisms melting at 75—76·5°; the *ethoxy*-derivative melts at 58—60°. The *acetyl* compound crystallises from ethyl acetate in fine, white needles, which melt at 73—74°, whilst the *benzoyl* compound, obtained by Einhorn and Hollandt's benzoylation method, forms long, white crystals melting at 142—143°.

β : ?-Dibromo-α-hydroxydihydroisoapiole,

$$CH_2<^{O}_{O}>C_6Br(OMe)_2\cdot CH(OH)\cdot CHMeBr,$$

prepared from bromo*iso*apiole dibromide, separates from alcohol in large, well-defined crystals melting at 85—86°. The *methoxy*- and *ethoxy*-compounds melt at 92—93° and 72—73° respectively. Its *acetyl* derivative crystallises with difficulty and melts at 114—115°; the *benzoyl* derivative melts at 117—118°.

When β : ?-dibromo-α-hydroxydihydro*iso*apiole is boiled with alcoholic potash, *bromo-α-ketodihydroisoapiole*,

$$CH_2<^{O}_{O}>C_6Br(OMe)_2\cdot CO\cdot CH_2Me,$$

is formed; it crystallises from alcohol and melts at 128—129°. The ethers of β : ?-dibromo-α-hydroxydihydro*iso*apiole, on the other hand, are not affected by alcoholic potash. A. McK.

o-Hydroxylamino-, o-Nitroso-, and o-Azoxy-benzyl Alcohols. Eugen Bamberger (*Ber.*, 1903, 36, 836—840).—*o-Hydroxylaminobenzyl alcohol*, $OH\cdot NH\cdot C_6H_4\cdot CH_2\cdot OH$, crystallises from boiling water in colourless, glistening flakes, melts at 104·2—104·7°, reduces Fehling's solution, oxidises in air to azoxybenzyl alcohol, and with diazobenzene chloride yields the compound $OH\cdot CH_2\cdot C_6H_4\cdot N(OH)\cdot N_2\cdot Ph$.

o-Azoxybenzyl alcohol, $C_{14}H_{14}O_3N_2$, forms pale straw-yellow, long, silky needles and melts at 123°.

o-Nitrosobenzyl alcohol, $NO\cdot C_6H_4\cdot CH_2\cdot OH$, crystallises from hot acetone or chloroform in pale yellow, almost colourless, minute, short needles, melts at 101° to a greenish-yellow liquid, condenses with aromatic amines to azo-compounds, and quantitatively with hydroxylaminobenzyl alcohol to azoxybenzyl alcohol.

Nitrosobenzyl alcohol is converted by boiling with water into azoxybenzyl alcohol and anthranil. T. M. L.

Does Cholesterol occur in Maize Oil? Augustus H. Gill and Charles G. Tufts (*J. Amer. Chem. Soc.*, 1903, 25, 251—254).—The alcoholic extract of maize oil was hydrolysed by potassium

hydroxide and a product was obtained which, after crystallisation from alcohol, melted at 137·5—138°. This substance is different from cholesterol, which melts at 146—147°, but is possibly identical with Burian's sitosterol (Abstr., 1898, i, 72). A. McK.

Betasterol. A. Rümpler (*Ber.*, 1903, 36, 975—976).—*Betasterol*, $C_{26}H_{44}O$, a cholesterol isolated from beetroot (compare this vol., i, 214), crystallises from a mixture of alcohol and ether in clusters of small needles, is optically inactive, and melts at 117°. On remelting after solidification, the melting point sinks to 112°, and on repeating the process, to 98° without any apparent decomposition. Betasterol unites with bromine and shows all the ordinary reactions of cholesterols. The chloroform solution becomes reddish-violet when shaken with concentrated sulphuric acid, whilst the acid is coloured a bluish-red, both solutions showing a green fluorescence. The solution in acetic anhydride becomes a dark violet-blue on addition of concentrated sulphuric acid, changing gradually to brown, the change being instantaneous on addition of water. E. F. A.

Syntheses by means of Carbonyl Sulphide. Fritz Weigert (*Ber.*, 1903, 36, 1007—1013).—On bringing magnesium organic compounds together with carbonyl sulphide, (i) thio-acids and (ii) *s*-trisubstituted carbinols are formed in varying proportions. Thus, ethyl bromide, phenyl bromide, and *p*- and *o*-tolyl bromides form thiolpropionic, thiolbenzoic, *p*- and *o*-thioltoluic acids on the one hand, and triethyl- and triphenyl-carbinols on the other; tritolyl carbinol is not produced in quantity. p-*Thioltoluic acid*, $C_6H_4Me\cdot CO\cdot SH$, crystallises in faint green, oblique prisms melting at 43—44°. Iodine oxidises it to p-*tolyl disulphide*, which crystallises from alcohol in long, flat prisms melting at 116°. o-*Thioltoluic acid* was only obtained as a yellow oil. o-*Tolyl disulphide* forms short, oblique prisms melting indistinctly at 75°. E. F. A.

***iso*Cinnamic Acid.** Arthur Michael and W. W. Garner (*Ber.*, 1903, 36, 900—908. Compare Abstr., 1902, i, 32, and Liebermann, this vol., i, 255).—The so-called *iso*cinnamic acid is not formed when β-bromo*allo*cinnamic acid is reduced with zinc filings and absolute alcohol; the presence of a small amount of water appears to be necessary. The character of the zinc is also an important factor in the reduction, as with certain specimens, no *iso*-acid melting at 36° could be obtained. Many of the properties of the *iso*-acid can be accounted for by the assumption that it is a mixture of one part of hydrocinnamic acid and two parts of *allo*cinnamic acid; for example, melting point, solubilities of some of its salts, and its reaction with potassium permanganate. The analytical data and the almost complete transformation of the *iso*-acid into the *allo*-acid by means of the aniline salt are not in harmony with this assumption.

The calcium salt contains 2 and not $3H_2O$. J. J. S.

Constitution of the Acid $C_{16}H_{14}O_3$ obtained by the Reduction of α-Oxydiphenylbutyrolactone. Emil Erlenmeyer, jun., and Arbenz (*Ber.*, 1903, 36, 916—919. Compare Abstr., 1898, i, 668; 1902, i, 543).—The acid $C_{16}H_{14}O_3$ reacts with a chloroform solution of

bromine to yield a *dibromide*, which readily loses a molecule of hydrogen bromide, yielding a brominated lactone. Both compounds, when boiled with water or alcohol, yield α-oxydiphenylbutyrolactone.

When the acid is boiled with sodium hydroxide solution, it is hydrolysed to dibenzyl and oxalic acid.

These reactions can best be explained by the following constitutional formula for the acid $C_{16}H_{14}O_3$, namely, $CHPh{:}CPh{\cdot}CH(OH){\cdot}CO_2H$.

J. J. S.

Direct Migration of Hydroxyl Groups from the α- to γ-Positions. Emil Erlenmeyer, jun. (*Ber.*, 1903, **36**, 919—923).—The *α-oxylactone*, $C_{19}H_{18}O_3$, obtained by suspending phenylpyruvic acid and cumene in concentrated hydrochloric acid, saturating with hydrogen chloride, and leaving for 5—6 days in the summer, crystallises from alcohol in large, colourless plates melting at 186°. When the reaction is carried out during the winter months, it proceeds more slowly, and a second modification of the oxylactone is obtained; it melts at 198°, crystallises in needles, and is transformed into the former compound by boiling with acetic acid.

Reduction with sodium amalgam gives rise to a *hydroxylactone* melting at 169°. This is not affected by prolonged boiling with hydrochloric acid. Zinc dust and acetic acid transform the hydroxylactone into an unsaturated *lactone*, $C_{19}H_{18}O_2$, melting at 124°, together with an *acid*, $C_3H_7{\cdot}C_6H_4{\cdot}CO{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, melting at 111°. The zinc cake, when treated as described by Lux (Abstr., 1898, i, 669), yields an *acid*, $C_3H_7{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CH(OH){\cdot}CO_2H$, melting at 136°. This combines with bromine, and when the bromine derivative is boiled with alcohol the two stereoisomeric lactones are re-formed. The α-hydroxy-β:γ-unsaturated acid is transformed into the unsaturated lactone and also into the γ-ketonic acid melting at 111° when boiled with 12 per cent. hydrochloric acid. It is shown that the *rationale* of this transformation consists in the direct removal of the hydroxyl group from the α- to the γ-position and the shifting of the double bond.

J. J. S.

Colloidal Indigotin. Richard Möhlau and M. R. Zimmermann (*Zeit. Farb. Text. Chem.*, 1903, **2**, 25—26).—A solution of colloidal indigotin is obtained by reducing indigotin with an alkaline solution of sodium hyposulphite, adding lysalbic or protalbic acid to the solution, air being excluded, and, after filtration, oxidising at 0° by means of hydrogen peroxide; the liquid so obtained can be preserved for any length of time, and can be evaporated to dryness without the indigotin undergoing conversion into the hydrosol-form. Organic acids produce with the solution a blue, flocculent precipitate, which forms either at once or gradually, according to the concentration; ammonia, alkalis, and their salts produce no precipitate, but alcohol, acetone, or pyridine cause indigotin to separate.

If other colloids, such as dextrin, gelatin, or gum, be used in place of lysalbic or protalbic acids, only ordinary indigotin is obtained; it is, therefore, probable that in the colloidal form indigotin is combined with the acids.

W. A. D.

Some Derivatives of 2-Hydroxy-α-naphthoic Acid. F. BODROUX (*Compt. rend.*, 1903, **136**, 617—618).—It has already been shown (this vol., i, 344) that by the action of magnesium and then of carbon dioxide the ethers of *p*-bromophenol are converted into the corresponding ethers of *p*-hydroxybenzoic acid. By the same process, the following derivatives of α-naphthoic acid have been obtained in a yield of about 20 per cent.

2-*Methoxy-α-naphthoic acid*, $OMe\cdot C_{10}H_6\cdot CO_2H$, crystallises from 90 per cent. alcohol in short prisms and melts at 176°. 2-*Ethoxy-α-naphthoic acid* crystallises from dilute alcohol in thin plates, melts at 142°, and decomposes at 160°. 2-*Propyloxy-α-naphthoic acid* crystallises from alcohol in long, white needles, melts at 79°, and begins to decompose at 145°. These three acids are soluble in the common organic solvents except light petroleum. When heated with a concentrated aqueous solution of hydrobromic acid, carbon dioxide is evolved and the ether of β-naphthol which is produced is then hydrolysed. J. McC.

Transformation of Lævulic Acid into Derivatives of *cyclo*Pentadiene. PAUL DUDEN and R. FREYDAG (*Ber.*, 1903, **36**, 944—952).—1-*Carboxy*-4-*methyl*cyclo*pentadiene*-2-*propionic acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot C{<}{\substack{C(CO_2H)\\ CH{:}CMe}}{>}CH_2,$$

obtained by condensing 2 mols. of ethyl lævulate with sodium ethoxide in absolute alcoholic solution and hydrolysing the monoethyl ester thus formed by boiling it with a solution of sodium hydroxide (1 : 6) for 5—10 minutes, crystallises from methyl alcohol or glacial acetic acid in small, crossed prisms and melts at 218°; its alkali salts are easily soluble in water, and the *barium* salt forms a slightly yellow, crystalline mass. The *monoethyl ester*, $C_{12}H_{16}O_4$, which is the original product of the sodium ethoxide condensation described above, crystallises from light petroleum in long needles, melts at 103—104°, and is easily hydrolysed by aqueous alkali; the *dimethyl ester*, $C_{12}H_{16}O_4$, prepared from the acid by means of phosphorus pentachloride and methyl alcohol, is a viscid, colourless oil, which boils at 290° under the ordinary and at 185° under 20 mm. pressure. On adding bromine (2 atoms) to a chloroform solution of the dimethyl ester, a *dibromide* is formed which immediately loses hydrogen bromide, giving a *monobromo*-derivative crystallising from light petroleum in long needles and melting at 67°.

When the acid melting at 218° is heated in a vacuum at 220°, it loses carbon dioxide and is converted into 4-*methyl*cyclo*pentadiene*-2-*propionic acid*, $C_9H_{12}O_2$, which crystallises from light petroleum in long, felted needles and melts at 64—65°. If the decomposition of the acid is carried out under atmospheric pressure at 220°, preferably in a stream of hydrogen, 2 mols. of carbon dioxide are lost, and 4-*methyl*-2-*ethyl*cyclo*pentadiene* formed; it boils at 135° and is thereby slightly polymerised to an oil boiling at about 260°.

1-*Carboxy*-4-*methylfulvene*-2-*propionic acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot C{<}{\substack{C(CO_2H)\\ CH{:}CMe}}{>}C{:}CH_2,$$

obtained by condensing 1-carboxy-4-methyl*cyclo*pentadiene 2-propionic acid with aqueous formaldehyde, crystallises from methyl alcohol in thick, yellow plates and melts and decomposes at 187°; 1-*carboxy*-6-*phenyl*-4-*methylfulvene*-2-*propionic acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot C{<}{\scriptstyle C(CO_2H) \atop \scriptstyle CH:CMe}{>}C:CHPh,$$

obtained similarly by using benzaldehyde, crystallises from methyl alcohol in red needles and decomposes at 203°.

The foregoing facts are best in accord with the formula given above for the acid melting at 218°, but the constitution

$$CO_2H\cdot CH_2\cdot C{<}{\scriptstyle CMe\cdot CH_2 \atop \scriptstyle \text{———}CMe}{>}C\cdot CO_2H$$

is also possible; that the acid contains a methylene group and is not a $\Delta^{1:4}$-dihydro-2 : 5-dimethylterephthalic acid is shown by its easily losing carbon dioxide when heated, by its combining with formaldehyde and benzaldehyde, and by its yielding dyes with diazonium salts; moreover, it cannot be oxidised to 2 : 5-dimethylterephthalic acid.

W. A. D.

Tautomerism, especially in the Semicyclic 1 : 3-Diketone of the Pentamethylene Series. Hans Stobbe [and, in part, Arthur Werdermann] (*Annalen*, 1903, **326**, 347—370).—Just as ethyl succinate condenses with $\alpha\beta$-unsaturated ketones (Abstr., 1901, i, 147), so does benzylideneacetophenone give, with ethyl succinate, γ-phenyl-γ-phenacylglutaric acid. When an ethereal solution of the methyl ester of this acid is treated with solid sodium methoxide, a ring is formed with elimination of methyl alcohol, *methyl* 2-*benzoyl*-3-*phenyl*-cyclo*pentanone*-4-*carboxylate*, ${CHBz\cdot CHPh \atop CO\text{———}CH_2}{>}CH\cdot CO_2Me$, being produced; the ester melts at 115—116°, and, when treated with alkalis or acids, undergoes a cleavage of the ring, phenylphenacyl glutaric acid being re-formed; under no circumstances is a *cyclo*pentanone derivative produced, a behaviour analogous with that of other semicyclic 1 : 3-diketones (compare von Baeyer, Abstr., 1896, i, 245; and Leser, Abstr., 1902, i, 261).

The solid ester, from whatever solvent it has separated, is always a true diketone, as it shows no anomalous absorption of rapid electrical vibrations, has no acid properties, and when dissolved in a cold solvent gives no immediate coloration with ferric chloride. The change of the ketonic to the enolic form in solution has been very carefully followed. For this purpose, the depth of the tint given on addition of ferric chloride to solutions of definite and, therefore, comparable concentration is taken as the estimate of the extent of the change. Seven different shades are distinguished, varying from yellowish-brown to dark violet, and denoted by numbers. By this means, the influence of (1) the presence of various electrolytes, (2) the temperature, (3) the solvent, on the isomeric change has been studied. After preliminary experiments had shown that, firstly, after the addition of ferric chloride to a freshly prepared dilute alcoholic solution of the diketone, the coloration reached a maximum in eight hours, and,

secondly, that in the absence of ferric chloride the maximum depth of tint was not attained until after 96 hours, the effect of the addition of three drops of an $N/10$ solution of hydrochloric acid, potassium chloride, acetic acid, or sodium acetate on the transformation of a 0·1 per cent. alcoholic solution of the diketone was investigated. The two former substances were entirely without effect, but the two latter effected a rapid change, the maximum tint being reached in three hours. This result offers a marked contrast to Wislicenus' observations (Abstr., 1900, i, 37); he found that dibenzoylmethane changed very rapidly into α-hydroxybenzylideneacetophenone under the influence of hydrogen chloride, but was not affected by acetic acid.

The experiments just quoted were carried out at the ordinary temperature; at a higher temperature, the change was nearly instantaneous. A series of experiments carried out at 0° in the presence of the same four reagents showed that the change was only complete in the presence of sodium acetate after three days, whereas in the presence of hydrochloric acid the maximum tint was only given after 10 days. At the temperature of a boiling mixture of ether and carbon dioxide, no change of the ketonic into the enolic form was observed.

The influence of the solvent has been investigated by Wislicenus's (Abstr., 1900, i, 9) method, using the four solvents, alcohol, ether, benzene, and chloroform. The isomeric change takes place most rapidly in alcoholic solution, being nearly complete in 24 hours, less rapidly in ether when the tint had only attained the fourth shade in 24 hours, and still less rapidly in benzene; in chloroform, no change occurred in 48 hours. These results are in accordance with those of previous observers; water, alcohol, and ether act as catalytic accelerators of isomeric change, whilst benzene and chloroform preserve the existing state. A list is given of those substances the ketonic forms of which change into the enolic forms when in solution in the first class of solvents, and also of those substances in which the enolic is the labile form. Attention is drawn to the two substances which show an exceptional behaviour, namely, ethyl γ-diacetylsuccinate, the ketonic form of which rapidly changes into the enolic form in all solvents, and γ-angelicalactone, which at the ordinary temperature is stable in all solvents.

Alkalis rapidly effect the isomeric change of the ketonic into the enolic form, which dissolves with a yellow coloration; after a short time, the yellow colour disappears owing to the conversion of the diketone into a salt of phenylphenacylglutaric acid; the *sodium* salt, $C_{19}H_{16}O_5Na_2$, of this acid crystallises in anhydrous slender needles. So readily does this fission of the ring take place that all attempts, such as treatment of an ethereal solution of the diketone with alcoholic sodium methoxide, did not yield the sodium derivative of the keto-enolic form; this method gave, besides the glutaric acid (m. p. 175—177°), methyl γ-phenyl-γ-phenacylglutarate,

$$CHBz{\cdot}CHPh{\cdot}CH(CO_2Me){\cdot}CH_2{\cdot}CO_2Me,$$

melting at 75—77°. The *copper* salt of the keto-enolic form, $(C_{20}H_{17}O_4)_2Cu$, slowly separates when alcoholic copper acetate is added to a dilute alcoholic solution of the diketone; as the copper salt is completely insoluble in alcohol, the diketone is in time entirely pre-

cipitated from its alcoholic solution by this means. The formation of this copper salt from the ketonic form is explained by the observation above recorded, that the ketonic changes into the enolic form in alcoholic solution, especially rapidly in the presence of acetates. Many other ketonic forms behave in a similar manner, whilst others have not this property.

Attempts to isolate the keto-enolic form from its solutions by the action of sulphuric acid, or by the action of heat (melting), or from its salts, lead only to the production of a pasty mass which at first gave a coloration with ferric chloride, but after a short time solidified to crystals of the pure ketonic form. K. J. P. O.

Derivatives of 1:3-Diketones containing Nitrogen. HANS STOBBE and ARTHUR WERDERMANN (*Annalen*, 1903, **326**, 371—379. Compare preceding abstract).—Under all conditions, methyl 2-benzoyl-3-phenyl*cyclo*pentanone-4-carboxylate yields only a mono-oxime, which crystallises in colourless needles melting at 184—185° and has feebly acid properties, dissolving slowly in cold aqueous sodium hydroxide and forming yellowish-green solutions of salts when treated with alcoholic solutions of bases. If ferric chloride is added to an alcoholic solution of the oxime, a pale green colour develops after a few seconds, which in a short time deepens to a dark green; when, however, ferric chloride is added to a solution of a yellowish-green salt of the oxime, a cherry-red coloration immediately appears. This red colour is obtained when alkali is added to the dark green solution just mentioned; further, the cherry-red colour is changed into dark green by adding acid; the green iron salt exists in acid and the red iron salt in alkaline solution. Two differently coloured iron salts have been observed in the case of substances with an analogous constitution. Attention is drawn to the fact that the tendency of 1:3-diketones to form mono-oximes or di-oximes bears no relation to the constitution of the substance taken as a whole, but depends mainly on the conditions of experiment.

The semicarbazone of this diketone (m. p. 232°; Abstr., 1901, i, 147) gives reactions with ferric chloride similar to those observed in the case of the oxime; the alcoholic solution of the semicarbazone becomes yellow when it is made alkaline, and develops, on addition of ferric chloride, at first a pale green and then a dark or a bluish-green coloration. Whether the semicarbazide attacks the carbonyl group in the pentane ring or the carbonyl group which forms part of the benzoyl group could not be decided. When boiled with excess of 30 per cent. sulphuric acid, fission of the ring follows, with the formation of γ-phenyl-γ-phenacylglutaric acid (m. p. 175°). On boiling with concentrated alcoholic sodium hydroxide, the semicarbazone is merely hydrolysed, the *acid*, $\begin{matrix} NH_2\cdot CO\cdot N_2H\!:\!CPh\cdot CH\cdot CHPh \\ CO\text{——}CH_2 \end{matrix}\!\!>\!CH\cdot CO_2H$, being formed; this acid, in which the position of the semicarbazone residue is uncertain, melts and decomposes at 236—237°; its *sodium* salt is sparingly soluble, and its *silver* salt, $C_{20}H_{18}O_4N_3Ag$, very sensitive to light.

The *phenylpyrazole* of methyl 2-benzoyl-3-phenyl*cyclo*pentanone-4-carboxylate, $N{<}\begin{matrix}CPh{-}C{\cdot}CHPh\\ \| \\ NPh{\cdot}C{-}CH_2\end{matrix}{>}CH{\cdot}CO_2Me$ or

$$NPh{<}\begin{matrix}CPh{:}C{\cdot}CHPh\\ | \\ N{=\!=}C{-}CH_2\end{matrix}{>}CH{\cdot}CO_2Me,$$

is prepared by the action of phenylhydrazine on the cold alcoholic solution of the diketone, and crystallises in needles melting at 149—150°, which very readily decompose when kept moist, give Knorr's pyrazoline reaction (Abstr., 1893, i, 229), and no coloration with ferric chloride and concentrated sulphuric acid. The formation of the pyrazole contrasts with the production of phenylhydrazides alone from cyclic β-ketonic esters of the pentamethylene series (Abstr., 1901, i, 539). K. J. P. O.

Amino-derivatives of Phthalic Acid. ARNALDO PIUTTI and G. ABATTI (*Ber.*, 1903, **36**, 996—1007).—The amino-derivatives of phthalic acid are only obtained crystalline in the carbonyl form, $CO_2H{\cdot}R''{\cdot}CO{\cdot}NH{\cdot}C_6H_4R'$, although the iron chloride reaction shows that the tautomeric enolic form is also present in solution. They decompose very easily, forming the corresponding imides.

The imides are obtained either as colourless or yellow substances, melting closely together and changing one into the other very easily, even in neutral solvents. They are believed to be dimorphous.

p-*Methoxyphenylphthalimide* forms colourless, rhombic crystals [$a:b:c = 1{\cdot}0096:1:1{\cdot}0464$], becoming yellow at 140—145°, again colourless at about 155°, and melting at 162°. The yellow form becomes colourless at 158·5° and melts at 161·5°.

p-*Methoxyphenylhydrophthalimide* forms a white modification, which, when slowly heated, becomes yellow at 75—80° and melts at 108°; when heated quickly, it melts at 95°. The yellow modification melts at 108° and crystallises in monoclinic rhombs [$a:b:c = 1{\cdot}3347:1:1{\cdot}16596$; $\beta = 87°49'$].

Of the other substances prepared, the following are new. p-*Methoxyphenylphthalamic acid*, $C_{15}H_{13}O_4N$, melts at 180—185°; the corresponding *ethoxy*-compound melts at 160—165°. *Phenyl-Δ^1-hydrophthalamic acid*, $C_{14}H_{15}O_3N$, melts at 155°. p-*Hydroxyphenyl-Δ^1-hydrophthalamic acid* melts at 170—175°; the corresponding *methoxy*- and *ethoxy*-compounds melt at 150—155° and at about 145° respectively. E. F. A.

Condensation Products of $\Delta^{1:4}$-Dihydroterephthalic Acid. JOHANNES THIELE and OSCAR GIESE (*Ber.*, 1903, **36**, 842—845).—The readiness with which *cyclo*pentadiene, indene, and fluorene condense with aldehydes and ethyl oxalate in the presence of sodium ethoxide (Marckwald, Abstr., 1895, i, 535; Wislicenus, Abstr., 1900, i, 349; and Thiele, Abstr., 1900, i, 298, 347; 1901, i, 76) depends on the presence of the five-membered ring, $CH_2{<}\begin{matrix}C{:}C\\ | \\ C{:}C\end{matrix}$, as neither tropilidene (Abstr., 1902, i, 145), dihydronaphthalene, diphenylmethane, nor similar substances are able to condense in such a manner. On the other hand, methyl $\Delta^{1:4}$-dihydroterephthalate, which has this grouping,

condenses readily with aldehydes and ethyl oxalate, just as do ethyl glutaconate and ethyl crotonate.

Phthalidedicarboxylic acid, $\begin{array}{l}CO\cdot C_6H_3\cdot CO_2H \\ | \quad\;\; | \\ O—CH\cdot CO_2H\end{array}$, is prepared by adding a solution of ethyl oxalate and sodium ethoxide in absolute alcohol to methyl dihydroterephthalate suspended in alcohol; after a short time, the ester is hydrolysed with potassium hydroxide, the unchanged terephthalic acid precipitated by acid after adding water, and then the lactonic acid extracted by ethyl acetate; it forms crystals which lose carbon dioxide at 240°, passing into the lactone of ω-hydroxymethylterephthalic acid, $CO_2H\cdot C_6H_3 <\begin{smallmatrix}CH_2\\ CO\end{smallmatrix}> O$, which melts at 283—284°.

Anisylterephthalic acid, $OMe\cdot C_6H_4\cdot CH_2\cdot C_6H_3(CO_2H)_2$, is prepared in a similar manner from methyl dihydroterephthalate and anisaldehyde in the presence of sodium methoxide in methyl alcoholic solution; it crystallises in colourless needles melting at 265—266°.

K. J. P. O.

Preparation of Nitrosobenzaldehyde. FREDERICK J. ALWAY (*Ber.*, 1903, 36, 793—794).—Three compounds are produced when *p*-nitrobenzaldehyde is reduced with zinc dust and acetic acid: (i) the *N-p*-formylphenyl ether of *p*-nitrobenzaldoxime,

$$NO_2\cdot C_6H_4\cdot CH <\begin{matrix}O\\ |\\ N\cdot C_6H_4\cdot CHO\end{matrix},$$

(ii) a red, insoluble compound, which is apparently the corresponding azoxy-compound, $N_2O\left(C_6H_4\cdot CH <\begin{matrix}O\\ |\\ N\cdot C_6H_4\cdot CHO\end{matrix}\right)_2$, (iii) a yellow substance of unknown constitution which seems to be a condensation product of *p*-hydroxylaminobenzaldehyde. The same substances are produced by the electrolytic reduction of *p*-nitrobenzaldehyde dissolved in concentrated sulphuric acid. The proportions in which the three compounds are produced depends on the conditions, but all three are oxidised by chromic acid to nitrosobenzaldehyde. T. M. L.

Action of Sodium Hydroxide on Nitrobenzaldehyde. RICHARD SELIGMAN (*Ber.*, 1903, 36, 818—819).—*o*-, *m*-, and *p*-Nitrobenzaldehydes dissolve without decomposition in dilute aqueous sodium hydroxide, yielding solutions which are nearly colourless. When kept, or when stronger alkali is employed, decomposition into the acid and alcohol occurs. T. M. L.

***sym*-Trinitrobenzaldehyde.** FRANZ SACHS and WILLIBALD EVERDING (*Ber.*, 1903, 36, 959—962. Compare Abstr., 1902, i, 377, 682).—2 : 4 : 6-*Trinitrobenzaldehyde dimethylaminoanil*,

$$C_6H_2(NO_2)_3\cdot CH:N\cdot C_6H_4\cdot NMe_2,$$

prepared by the interaction of 2 : 4 : 6-trinitrotoluene and nitrosodimethylaniline, dissolved in acetone in presence of sodium carbonate, crystallises in black, rhombic plates exhibiting a bronze-green reflex and appearing ruby-red in transmitted light, is sparingly soluble in most

solvents, forming reddish-violet solutions, but dissolves in ethylic benzoate forming a deep blood-red liquid.

2 : 4 : 6-*Trinitrobenzaldehydephenylhydrazone* crystallises in reddish-brown needles melting at 202°. The *phenylbenzylhydrazone* melts at 161°. The p-*nitrophenylhydrazone* crystallises from acetone in bright red needles melting at 247°. The *anil* forms yellowish-red needles melting at 162°. The *oxime* melts at 158°. Ammonium sulphide reduces the aldehyde to *dinitroaminobenzaldoxime* melting at 243°. When a solution of the aldehyde in benzene is exposed to sunlight, a brownish-yellow precipitate is formed, which the author believes to be a compound of benzene with 4 : 6-*dinitro*-2-*nitrosobenzoic acid*.

E. F. A.

Intermolecular Transpositions in the Synthesis of Aromatic Aldehydes by Gattermann's Method. Derivatives of *p*-Dimethylbenzaldehyde. LUIGI FRANCESCONI and C. M. MUNDICI (*Gazzetta*, 1902, 32, ii, 467—494).—The compound described by Harding and Cohen (Abstr., 1901, i, 725) as 2 : 5-dimethylbenzaldehyde is, in reality, 2 : 4-dimethylbenzaldehyde; the corresponding oxime melting at 83·5—84° and the acid melting at 124—125° have also the two methyl groups in the *m*-position. Hence, in the preparation of an aldehyde from *p*-toluene by Gattermann's reaction, one of the methyl groups becomes displaced from the para- to the meta-position with respect to the other, and the aldehyde group enters in the vacant place.

2 : 5-Dimethylbenzaldehyde was prepared by Bouveault (Abstr., 1897, i, 530; and 1898, i, 585). It forms two oximes: (1) the *anti-oxime*, $\begin{matrix} C_6H_3Me_2\cdot CH \\ OH\cdot N \end{matrix}$, prepared by gradually adding a concentrated solution of hydroxylamine hydrochloride to a mixture of the aldehyde with excess of sodium hydroxide solution, crystallises from light petroleum in either thin plates or prisms, melts at 62·5—63·5° and dissolves in the ordinary organic solvents; the *sodium* derivative is gelatinous and soluble in water. This oxime reacts with amyl nitrite yielding *azodimethylbenzenyl peroxide*,

$$C_6H_3Me_2\cdot CH\colon N\cdot O\cdot O\cdot N\colon CH\cdot C_6H_3Me_2,$$

which separates in small crystals melting and decomposing at 97—98°; it dissolves readily in chloroform and slightly in ether. (2) The *syn-oxime*, $\begin{matrix} C_6H_3Me_2\cdot C\cdot H \\ N\cdot OH \end{matrix}$, obtained by the action of dry hydrogen chloride on the *anti*-oxime in ethereal solution, crystallises from a mixture of ether and light petroleum in long, shining needles, melts at 133° and is moderately soluble in chloroform or benzene; when distilled under reduced pressure, it is converted into the *anti*-compound. The *anti*-oxime, when treated with acetic anhydride, yields the corresponding acetyl derivative, which is gradually decomposed by water with the evolution of an odour of carbylamine. The *syn*-oxime, however, does not yield an acetyl compound, but p-*dimethylbenzonitrile* [$Me_2 : CN = 1 : 4 : 3$], which is also obtained by the fractional distillation, under reduced pressure, of the acetyl compound of the *anti*-oxime; the nitrile forms a white, crystalline mass melting at 13—14·5°.

p-*Dimethylbenzyl acetate* [$Me_2 : CH_2 \cdot OAc = 1 : 4 : 3$] is obtained, together with a crystalline *compound* melting at 151—153°, when 2 : 5-dimethylbenzaldehyde is heated with concentrated acetic acid, zinc dust, and a few drops of copper chloride solution, and forms a colourless liquid boiling at 242—243°. When treated with alcoholic potassium hydroxide solution, it yields :

2 : 5-*Dimethylbenzyl alcohol*, a colourless liquid boiling at 232—234°; this alcohol is also obtained when the aldehyde is treated with either sodium amalgam and water or aqueous potassium hydroxide.

The application to *p* xylene of Gattermann's method for the synthesis of aldehydes is also described. T. H. P.

Reduction Product of the Polymeride of Diacetyl. II. Otto Diels and Hans Jost (*Ber.*, 1903, 36, 954—957. Compare Abstr., 1902, i, 744).—The ketone, $C_8H_{14}O$, obtained by the reduction of termolecular diacetyl with sodium amalgam, and purified by means of its bisulphite compound, boils at 169—170° under 769 mm. pressure, has a sp. gr. 0·8943 at 14°, 0·8899 at 22°, n_D 1·43587 at 22°, and a mol. refraction 37·05 (calc., 37·01); its p-*nitrophenylhydrazone* $C_{14}H_{19}O_2N_3$, forms yellow crystals and melts at 168°. The ketone is probably a dimethyl*cyclo*hexanone or a trimethyl*cyclo*pentanone.

W. A. D.

Ketonic Bases. Ernst Schmidt (*Arch. Pharm.*, 1903, 241, 116—121. Compare Abstr., 1899, i, 4).—The compounds obtained by the action of phosphorus pentachloride on the oximes of phenacyltrimethyl ammonium chloride (Abstr., 1898, i, 247) and pyridinephenacyl (pyridineacetophenone) chloride (Abstr., 1900, i, 688), $NR'''Cl \cdot CH_2 \cdot CPh\colon NOH$ [$R''' = Me_3$ or C_5H_5], are identical with the products obtained by adding trimethylamine or pyridine respectively to bromoacetoanilide and exchanging the bromine for chlorine (this vol., i, 410). Consequently they must have the constitution $NR'''Cl \cdot CH_2 \cdot CO \cdot NHPh$, and their formation from the oximes is a normal Beckmann transformation.

The substance obtained by the action of phosphorus pentachloride on *iso*quinolinephenacyloxime chloride (this vol., i, 365) really has the constitution $C_9H_7NCl \cdot CH_2 \cdot CCl_2 \cdot NHPh$, for it can be made by heating *iso*quinolinechloroacetoanilide (*loc. cit.*) with phosphorus pentachloride in the presence of phosphorus oxychloride. C. F. B.

Action of Aromatic Amines on 1 : 5-Dinitroanthraquinone. Felix Kaufler (*Zeit. Farb. Text. Chem.*, 1903, 2, 69—71).—When 1 : 5-dinitroanthraquinone is heated with an excess of an aromatic base of the type NH_2R, both nitro-groups are replaced by the radicle NHR; the nitrous acid initially formed then decomposes an equivalent quantity of base, as is shown by the theoretical quantity of nitrogen being evolved.

1 : 5-*Dianilinoanthraquinone*, $NHPh \cdot C_6H_3\colon(CO)_2\colon C_6H_3 \cdot NHPh$, prepared by heating the constituents at the boiling point of aniline, crystallises from amyl alcohol as a brownish-red mass, sinters at 180°, and melts at 190°. 1 : 5-*Di*-p-*toluidinoanthraquinone*, prepared from

p-toluidine, separates from alcohol on dilution with water in small, reddish-violet crystals and melts and decomposes at 200—210°. 1 : 5-*Di*-p-*hydroxyanilinoanthraquinone*, prepared by using *p*-aminophenol, was not obtained pure. 1 : 5-*Di*-p-*nitroanilinoanthraquinone*, formed on heating 1 : 5-nitroanthraquinone with *p*-nitroaniline at 250°, crystallises indefinitely from nitrobenzene and does not melt sharply. W. A. D.

Methylbromocamphor, Bromomethylcamphor, and Methylenecamphor. JULES MINGUIN (*Compt. rend.*, 1903, **136**, 751—753). —By the action of alcoholic potassium hydroxide on benzylbromocamphor, a benzylidenecamphor is obtained, identical with that prepared by the interaction of sodium camphor and benzaldehyde (this vol., i, 267). Using a similar reaction, other methylenecamphors can be prepared.

Methylbromocamphor, $C_8H_{14}<\begin{matrix}CBrMe\\|\\CO\end{matrix}$, prepared by the action of bromine on methylcamphor in solution in carbon disulphide, crystallises in orthorhombic prisms [$a : b : c = 0·76042 : 1 : 0·4921$; $\beta = 105°30'$], melts at 61°, and has $[\alpha]_D$ +176·8° in alcoholic solution ; it is reduced by zinc dust and alcohol to methylcamphor. When boiled with alcoholic potassium hydroxide, hydrogen bromide is eliminated, and *methylenecamphor*, $C_8H_{14}<\begin{matrix}C:CH_2\\|\\CO\end{matrix}$, is formed ; this melts at 30—35°, boils at 218°, and has $[\alpha]_D$ +127·5° ; it yields a viscous oxime and is oxidised by permanganate to camphoric acid. With hydrogen bromide, it forms an additive product which is *bromomethylcamphor*, $C_8H_{14}<\begin{matrix}CH·CH_2Br\\|\\CO\end{matrix}$, analogous to bromobenzylcamphor (*loc. cit.*) ; it crystallises in orthorhombic prisms

[$a : b : c = 0·76042 : 1 : 0·73996$; $\beta = 105°30'$],

melts at 65°, and has $[\alpha]_D$ +150·5° in alcoholic solution ; by zinc dust and alcohol, it is reduced to methylcamphor. K. J. P. O.

Thio-derivatives of Camphor. HENRI WUYTS (*Ber.*, 1903, **36**, 863—870).—Just as acetophenone and benzophenone, when treated with alcoholic ammonium sulphide, are converted into disulphides, $S_2(CHMePh)_2$ (Engler, Abstr., 1879, 61 ; Baumann and Fromm, Abstr., 1895, i, 363), so does camphor react with ammonium sulphide very slowly at the ordinary temperature, although more rapidly when heated under pressure with solid ammonium sulphide at 150° (compare Schlebusch, *Ber.*, 1870, **3**, 591). A mixture of *disulphide*, $S_2(C_{10}H_{17})_2$, and a *trisulphide*, $S_3(C_{10}H_{17})_2$, were obtained by heating camphor with solid ammonium sulphide and a little alcohol under pressure slowly up to 100° and then still more slowly to 150° ; all attempts at separation of these sulphides by recrystallisation failed ; fractions were obtained melting from 127—132° to 183—185°, and having a mol. weight 307—325 in benzene and 355—356 in naphthalene ; a preparation, which crystallised in colourless, feathery needles melting at 128—134°, had $[\alpha]_D$ +60°6′ at 15°. When distilled under the ordinary pressure, the

originally pale yellow liquid becomes red at 250°, and a red substance rapidly distils at 280—285°; distilled under 100 mm. pressure, the same red material is obtained, but under 15 mm. pressure *bornyl disulphide*, $S_2(C_{10}H_{17})_2$, passes over first and melts at 175—176°.

The red material is a mixture of thiocamphor and thioborneol; these are separated by adding to the alcoholic solution of the mixture an alcoholic solution of lead acetate, when the lead mercaptide is precipitated, leaving the thiocamphor in solution. Roughly, each compound is present to the amount of 50 per cent. of the mixture. *Thiocamphor*, $C_8H_{14}<\begin{matrix}CH_2\\ | \\ CS\end{matrix}$, forms salmon-red crystals from alcohol, melting at 118—119°, boiling at 104° under 15 mm. and at 228—230° under 761 mm. pressure, and having $[\alpha]_D$ $-41°42'$ at 15° in a 3·64 per cent. solution in ethyl acetate; its odour is not unpleasant; freely exposed to the air, it is rapidly oxidised, becoming colourless. When treated with phenylhydrazine, it is nearly quantitatively converted into camphorphenylhydrazone with evolution of hydrogen sulphide; under the action of hydroxylamine hydrochloride in the presence of sodium hydroxide, camphoroxime is formed (m. p. 117—118°).

Thiolborneol, $C_{10}H_{17}\cdot SH$, can be prepared from the lead mercaptide, obtained in the manner just mentioned, by treating a suspension of the latter in ether with acetic acid, or by reducing the mixed camphor sulphides, described above, by zinc dust and dilute hydrochloric acid, when bornyl disulphide is formed together with the thiolborneol; this compound forms crystals melting at 61—62°, boils at 98° under 15 mm. and at 224—225° under 760 mm. pressure, and has $[\alpha]_D$ $+21°5'$ at 15° in a 3·64 per cent. solution in ethyl acetate. The *lead mercaptide* is a yellow, insoluble powder, changing in colour at 250° and decomposing at 290°; the *mercury mercaptide* crystallises in long, white needles melting at 146—147° and is characteristic of thiolborneol. K. J. P. O.

Cyclic Terpenes and Camphor in the Animal System. III. Camphene in the Animal System. EMIL FROMM, HERMANN HILDEBRANDT, and PAUL CLEMENS (*Zeit. physiol. Chem.*, 1903, **37**, 189—202. Compare Abstr., 1902, i, 159, and 341).—Camphene is eliminated from the animal system in the form of *camphenglycolmonoglycuronic acid*, which has been isolated in the form of its *potassium* salt, $C_{16}H_{27}O_9K$. When heated at 105—110°, it appears to lose $\frac{1}{2}H_2O$. On hydrolysis with sulphuric acid, the glycuronic acid derivative yields a compound previously termed camphenol (Abstr., 1902, i, 159), but which is now shown to be identical with Bredt and Jagelki's camphenilanaldehyde, melting at 68—70° (Abstr., 1900, i, 134). When the crude aldehyde is distilled, it yields a small amount of a *compound*, $C_{20}H_{30}O$, crystallising in needles and melting at 72°. J. J. S.

Dextrorotatory Cadinene. ERNST DEUSSEN (*Arch. Pharm.*, 1903, **241**, 148).—With reference to Grimal's papers (this vol., i, 46, 185), the author points out that he had already isolated a *d*-cadinene (Abstr., 1900, ii, 579; 1902, i, 552). C. F. B.

Carana Elemi from Protium Carana. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1903, **241**, 149—159. Compare Abstr., 1902, i, 812).—The resin was collected in S.W. Venezuela. From its solution in ether, one per cent. aqueous ammonium carbonate extracted amorphous iso*careleminic acid*, $C_{40}H_{56}O_4$, which melts at 75°. Aqueous 1 per cent. sodium carbonate then extracted a mixture of acids; from a solution of the mixture in equal parts of ethyl and methyl alcohols, *careleminic acid*, $C_{40}H_{56}O_4$, crystallised; it melted at 215°; the mother liquor yielded amorphous *carelemic acid*, $C_{37}H_{56}O_4$, melting at 120°. From the remaining ethereal solution of the resin the ether was distilled off and the residue was distilled with steam; an *essential oil* came over, most of which boiled at 170—172°, but some at a higher temperature. From a solution of the residual resin in a mixture of ether and alcohol, *caramyrin*, $C_{30}H_{50}O$, crystallised; this was separated into α- and β-amyrins (identical with those obtained from other varieties of elemei) by the method used in the case of Manila elemi (*loc. cit.*); these melt at 181° and 192° respectively, the crystalline *monobenzoates* at 191°—192° and 229°. From the mother liquor of the caramyrin, amorphous *careleresen*, $C_{27}H_{40}O_2$, melting at 75—77°, was obtained. In 100 parts of the drug, there were contained *iso*careleminic acid, 2; careleminic acid, 8; carelemic acid, 10; essential oil, 10; amyrins, 20—25; resin, 30—35; impurities, 12—15.

C. F. B.

Degradation of Brazilin. WILLIAM H. PERKIN, jun. (*Ber.*, 1903, **36**, 840—842. Compare Abstr., 1902, i, 686, 815).—A reply to Kostanecki (this vol., i, 193).

K. J. P. O.

Olivil, its Composition and Constitution. GEORG KÖRNER and L. VANZETTI (*Atti R. Accad. Lincei*, 1903, [v], **12**, i, 122—125).—The formulæ which have been attributed to olivil are erroneous owing to the fact that this substance combines with most of its solvents, especially water and alcohols. Determination of the methoxy-groups in olivil shows that these contain one-tenth of the total carbon present, and this result, combined with the numbers obtained by the ultimate analysis, indicates the formula $C_{20}H_{26}O_8$. Confirmation is furnished by the formulæ of the compounds obtained by crystallising olivil from various alcohols, these being as follows: methyl alcohol, $C_{21}H_{28}O_8$; ethyl alcohol, $C_{22}H_{30}O_8$; propyl or *iso*propyl alcohol, $C_{23}H_{32}O_8$; all these compounds crystallise well and can be heated at 100° without losing alcohol, but by heating at 130—160° in a current of dry carbon dioxide the solvent is removed and the anhydrous compound obtained as a transparent, glassy mass melting at about 66°; when this is crystallised from dry acetone, benzyl alcohol, or trimethylcarbinol, it melts at 142·5° and has the composition $C_{20}H_{24}O_7$. When oxidised with permanganate, the acetyl derivative of olivil yields acetovanillic acid and a small proportion of acetovanillin, whilst dimethylolivil gives veratric and veratroylformic acids as principal products; in both cases, oxalic acid is also formed; when olivil is heated to a high temperature, it decomposes, yielding creosol among other products; dimethylolivil forms a diacetyl derivative. These facts indicate that olivil is a product of the condensation of coniferyl alcohol or an

isomeride of it, with the intervention of an oxygen atom, the position and function of which are as yet undetermined.

When olivil hydrate or alcoholate is heated with a dilute acid, preferably acetic acid, it is quantitatively transformed into an isomeride, *iso*olivil, which is both a di-phenol and a di-anisole. This transformation does not take place with the methyl or ethyl derivatives of olivil, and it has not been found possible to revert from *iso*olivil or one of its derivatives to the original olivil or its derivative. *iso*Olivil unites with various alcohols of crystallisation and with ethyl ether; it is more strongly dextrorotatory than olivil is lævorotatory; it forms well-crystallised mono- and di-alkyl derivatives, the former of which unite with water or alcohols of crystallisation. T. H. P.

Salts of the Hexone Bases with Picrolonic Acid. H. Steudel (*Zeit. physiol. Chem.*, 1903, 37, 219—220).—Arginine and histidine yield sparingly soluble salts with picrolonic acid (Knorr, 1897, i, 314). *Arginine picrolonate*, $C_{26}H_{26}O_{10}N_{12}$, obtained by the action of a concentrated alcoholic solution of picrolonic acid on an aqueous solution of arginine carbonate, forms long, sulphur-yellow needles melting and decomposing at 225°. One part dissolves in 1124 parts of water or in 2885 parts of 96 per cent. alcohol at the ordinary temperature.

Histidine picrolonate, $C_{26}H_{19}O_8N_{11}$, crystallises in small, pale yellow needles. Lysine does not yield a sparingly soluble compound with picrolonic acid. J. J. S.

Histidine. Reginald O. Herzog (*Zeit. physiol. Chem.*, 1903, 37, 248—249).—Histidine gives the characteristic biuret reaction. It gives negative results with the Zeisel-Herzig methoxy, and Herzig-Meyer methylimide, estimations. It reacts as a saturated compound towards the Baeyer-Willstätter reagent. On oxidation with barium permanganate, it yields hydrogen cyanide, carbon dioxide, ammonia, and a small amount of a crystalline substance.

With hydroxylamine and excess of hydrochloric acid, it yields a crystalline compound. J. J. S.

Transformation of Tropidine into Tropine. Albert Ladenburg (*Annalen*, 1903, 326, 379—380).—The tropidine used for the synthesis of tropine was absolutely pure and free from tropine (Abstr., 1890, 1167, 1333), and therefore the tropine synthesised in this manner was not originally present in the tropidine as suggested by Willstätter (this vol., i, 360). K. J. P. O.

Decacyclene (Trinaphthylenebenzene) and Dinaphthylenethiophen. Karl Dziewoński [with Paul Bachmann] (*Ber.*, 1903, 36, 962—971).—An intimate mixture of 100 grams of acenaphthene with 23 grams of finely-powdered sulphur contained in a globular ½-litre flask is slowly heated with a small flame; a lively action sets in at 205°, hydrogen sulphide being evolved, and the mass becoming brown. When the evolution of gas slackens, the fused mass is heated to about

290—294°, care being taken not to exceed this temperature until the action is at an end. The product is first extracted with alcohol to remove acenaphthene, and then with benzene, which dissolves out the dinaphthylenethiophen; the yellow, crystalline residue is afterwards extracted, first, once with toluene, then with xylene to remove all the thiophen; the residual decacyclene can be purified by crystallisation from cumene, and finally from nitrobenzene.

Decacyclene (*trinaphthylenebenzene*), $C_6(C_{10}H_6)_3$, forms large, glistening, golden-yellow needles melting at 387° and having a molecular weight of 450, as determined ebullioscopically. The *picrate* melts and decomposes at 295—296°.

Dinaphthylenethiophen, $C_{10}H_6<\begin{matrix}C—C\\ \| \quad \| \\ C\cdot S\cdot C\end{matrix}>C_{10}H_6$, crystallises from aniline or nitrobenzene in brilliant, red needles, melts at 278°, and sublimes in red needles at higher temperatures. The *picrate* contains 2 mols. of picric acid and melts at 250°. Naphthalic anhydride is formed on oxidation with chromic acid. The red colour is remarkable, as all other known homologues of thiophen are colourless. E. F. A.

Constitution of Anthranil. EUGEN BAMBERGER (*Ber.*, 1903, 36, 819—829).—A summary is given of the arguments for and against the formula $C_6H_4<\begin{matrix}N—\\ | \\ CH\end{matrix}>O$ for anthranil. It is held to be the only one by which all the known reactions of anthranil can be explained. T. M. L.

Oxidation of *o*-Aminobenzaldehyde to Anthranil. EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1903, 36, 829—836).—β-Substituted hydroxylamines condense with aldehydes to form *iso*aldoxime ethers, $R\cdot CH<\begin{matrix}NR'\\ | \\ O\end{matrix}$, and not amides, $R\cdot CO\cdot NHR'$. A condensation of *o*-hydroxylaminobenzaldehyde, $HO\cdot NH\cdot C_6H_4\cdot CHO$, to anthranil would therefore afford evidence in favour of the formula $C_6H_4<\begin{matrix}N—\\ | \\ CH\end{matrix}>O$, for anthranil.

o-Aminobenzaldehyde (82 grams) was oxidised by means of a neutral solution of Caro's persulphuric acid and gave 25 grams of anthranil; that this is formed from the *o*-hydroxylamino-compound is shown by the fact that no anthranilic acid is produced; moreover, there is no precedent for the oxidation of $\cdot CHO$ to $\cdot CO_2H$ by Caro's acid, although this agent readily oxidises $\cdot NH_2$ to $\cdot NH\cdot OH$. An important by-product (23 grams) was an iso-o-*hydroxylaminobenzaldehyde*, $C_7H_7NO_2$, which crystallises from boiling water in flat, white needles, melts at 129—129·5°, has a normal molecular weight in boiling acetone, gives a violet-blue coloration with ferric chloride, is acted on by sodium nitrite, behaves neither as an aldehyde nor as a substituted hydroxylamine, yields a neutral solution, but is dissolved by alkalis and reprecipitated in crystalline form by acids.

Other by-products were produced but not identified. T. M. L.

Action of Alkyl Iodides on the Indoles. I. New Syntheses and Characters of 1 : 3-Dimethyl-3-ethyl-2-methyleneindoline. GIUSEPPE PLANCHER (*Gazzetta*, 1902, 32, ii, 398—414. Compare Abstr., 1897, i, 102; 1898, i, 536; 1899, i, 452).—1 : 3-Dimethyl-3-ethyl-2-methyleneindoline may be prepared in a very pure form from 3-methylpentane-4-one (methyl α-methylpropyl ketone) by two methods: (i) by condensing its phenylhydrazone in presence of zinc chloride and treating the 2 : 3-dimethyl-3-ethylindolenine thus obtained with methyl iodide, and (ii) by condensing the phenylmethylhydrazone of the ketone with hydriodic acid; in either case, the hydriodide of the required substituted indoline is obtained.

The zinc chloride *compound* of 2 : 3-dimethyl-3-ethylindolenine, $(C_{12}H_{15}N)_2,ZnCl_2$, obtained as an intermediate product in the first of the above methods, separates from alcohol in colourless needles and is soluble in water, by which it is partially decomposed. 2 : 3-*Dimethyl-3-ethylindolenine picrate* crystallises from alcohol in pale yellow prisms which melt at 153°.

1 : 3-Dimethyl-3-ethyl-2-methyleneindoline hydriodide melts and decomposes at 244°, whilst the picrate separates from alcohol in faintly orange, yellow, monoclinic crystals [$a : b : c = 2·6202 : 1 : 1·3714$; $\beta = 85°26'$] melting at 123—124°. The benzoyl derivative, when heated with dilute hydrochloric acid, undergoes two distinct decompositions, partly splitting up into the dimethylethylmethyleneindoline and benzoic acid, whilst the remainder yields 1 : 3-dimethyl-3-ethylindolinone and acetophenone; therefore the benzoyl group must be attached to a carbon atom, probably the methylenic one, thus: $C_6H_4<{CMeEt \atop NMe}>C:CHBz$. The *acetyl* derivative, $C_{15}H_{19}ON$, separates from light petroleum in mammillary masses of a radiated, fibrous structure melting at 85—86°; on hydrolysis with dilute hydrochloric acid, it yields only the base and acetic acid. T. H. P.

Action of Alkyl Iodides on the Indoles. II. Transposition of Radicles in some Indolines. 3 : 3-Dimethyl-2 ethylindolenine and 1 : 3 : 3-Trimethyl-2-ethylideneindoline. GIUSEPPE PLANCHER and A. BONAVIA (*Gazzetta*, 1902, 32, ii, 414—446. Compare preceding abstract).—Methylation of 3-methyl-2-ethylindole yields 1 : 3-dimethyl-3-ethyl-2-methyleneindoline, the ethyl group migrating from the 2- to the 3-position; such a migration also occurs with the phenyl group in 2-phenylindole when this is methylated. In order to obtain light on the cause of this change in position, the authors have prepared 1 : 3 : 3-trimethyl-2-ethylideneindoline hydriodide, which they find is transformed into the isomeric 1 : 3-dimethyl-3-ethyl-2-methyleneindoline hydriodide on heating.

Experiments have also been made on the condensation of certain ketophenylhydrazones, the results of which lead to the following conclusions: (1) a ketophenylhydrazone containing the group ·NH·N:CMe·CH: yields only the corresponding indolenine on condensation; (2) one in which the grouping is

$$·NH·N:C(CH_2·)·CH:$$

gives both the corresponding indole and indolenine. (3) When the

grouping $\cdot NH\cdot N\colon CMe\cdot CH_2\cdot$ is present, the ketophenylhydrazone is capable of yielding two indoles on condensation, which takes place in preponderating amount by means of the $\cdot CH_2\cdot$ group.

The condensation of ethyl *iso*propyl ketone phenylhydrazone by means of zinc chloride yields: (1) 3-*Methyl*-2-iso*propylindole*, which boils at 175—177° under 30 mm., 184° under 38 mm., and at 288—290° under 755 mm. pressure and solidifies at the ordinary temperature to a faintly yellow, crystalline mass; the *picrate*,

$$C_{12}H_{15}N(C_6H_3N_2O_7),$$

separates from benzene in garnet-red needles which melt at 165—166°. (2) 3:3-Dimethyl-2-ethylindolenine, which crystallises from light petroleum in colourless prisms or scales melting at 52—53°, and is very soluble in most of the ordinary solvents; it is stable and has only feebly basic properties, although its salts undergo but slight hydrolysis; it does not attack permanganate in the cold; the *hydriodide* separates from alcohol in colourless leaflets melting at 186°; the *hydrochloride* is crystalline and the *benzoyl* derivative oily; the *picrate* is deposited from alcohol in pale yellow, triclinic plates [$a:b:c = 0{\cdot}7726:1:0{\cdot}9505$; $\alpha = 109°29'$; $\beta = 93°8'$; and $\gamma = 89°40'$] melting at 137—138°; oxidation of the base with permanganate appears to yield 3:3-dimethylindolenine-2-carboxylic acid, which then undergoes further change.

3:3-*Dimethylindolenyl 2-methyl ketoxime*,

$$C_6H_4{<}{\overset{CMe_2}{\underset{N}{\rule{2em}{0.4pt}}}}{\geqslant}C\cdot CMe\colon NOH,$$

obtained by the action of nitrous acid on 3:3-dimethyl-2-ethylindolenine, crystallises from benzene in colourless, monoclinic needles or prisms [$a:b:c = 1{\cdot}6884:1:0{\cdot}6656$; $\beta = 83°24'$] melting at 175—176°, and is soluble in alcohol or ether, and, to a slight extent, in light petroleum; it dissolves readily in alkali hydroxide solutions, giving yellow liquids from which carbon dioxide or feeble or dilute acids precipitate it unaltered; the *benzyl* derivative separates from dilute alcohol in colourless, well-defined needles melting at 77—78°; the *acetyl* compound, $C_{14}H_{16}O_2N_2$, is deposited from light petroleum in colourless, orthorhombic prisms [$a:b:c = 0{\cdot}5464:1:1{\cdot}0495$] melting at 149°. No conclusive evidence has been obtained as to whether the oxime has the anti- or syn-configuration.

1:3:3-*Trimethyl-2-ethylideneindoline*, $C_6H_4{<}{\substack{CMe_2\\ NMe}}{>}C\colon CHMe$, prepared either by the action of methyl iodide on 3:3-dimethyl-2-ethylindolenine or by the condensation of ethyl *iso*propyl ketone phenylmethylhydrazone in presence of hydriodic acid, boils at 257° under 757 mm. pressure and reddens in the air; in odour and other properties, it closely resembles trimethylmethyleneindoline; the hydriodide separates from alcohol in the dark in colourless, orthorhombic prisms [$a:b:c = 0{\cdot}7721:1:0{\cdot}3716$] melting at 185—186°; the *picrate* crystallises from alcohol in pale yellow scales melting at 107—108°; the *aurichloride* melts at 127°.

1:3:3-*Trimethyl-2-ethylindoline*, $C_6H_4{<}{\substack{CMe_2\\ NMe}}{>}CHEt$, obtained by

reducing 1 : 3 : 3-trimethyl-2-ethylideneindoline with zinc and hydrochloric acid, boils at 141° under 21 mm. pressure; the *picrate* is deposited from alcohol in pale yellow crystals melting at 185°.

The migrations of alkyl groups which occur when indole derivatives are alkylated are necessary consequences of the following facts. Every alkylideneindoline hydriodide is decomposed at a certain temperature into a 1 : 2 : 3-trialkylated indole and an alkyl iodide, and the latter products combine at some other temperature to form an alkylideneindoline hydriodide. The alkyl radicle originally eliminated in the form of iodide is always that from the 2-position, and to replace it the smallest radicle from the 3-position migrates to the 2-position. Of two isomeric hydriodides containing the same radicles differently arranged, that in which the heavier radicle is in the 2-position melts at a temperature 40—50° lower than its isomeride. The melting points of these hydriodides are not true melting points, but rather temperatures of decomposition; hence, the one having the higher melting point can be formed and exist at a temperature equal to or higher than the decomposition point of its isomeride. Hence, as soon as an alkyleneindoline hydriodide is resolved into a trialkylated indole and an alkyl iodide, the latter products recombine in another way, yielding an isomeric alkyleneindoline hydriodide. If, however, in preparing an alkyleneindoline hydriodide, the temperature is kept below its decomposition point, no such transformation will take place. T. H. P.

Formation of Betaines. FRITZ REITZENSTEIN (*Annalen*, 1903, **326**, 305—330).—The tendency of chloro-, dichloro-, and trichloroacetic acids to form betaines with tertiary amines has been investigated. After giving a *résumé* of the extensive literature on the subject, the author describes his own experiments, many of which are a repetition of the experiments of previous investigators.

Pyridine and trichloroacetic acid yield only the *salt*, which forms lustrous crystals melting at 112°, and no betaine; when treated with mercuric chloride, the salt gives the pyridine mercurichloride,

$$2C_5NH_5,3HgCl_2,$$

described by Monari (*Jahrb.*, 1884, 629).

Quinoline and trichloroacetic acid react very readily, the acid becoming decomposed into chloroform and carbon dioxide (Rhoussopoulos, Abstr., 1883, 96, 600), but when dilute alcoholic solutions of the two substances are left for some time, the *trichloroacetate* is obtained as a white, crystalline compound melting at 100°; on heating, the salt is rapidly decomposed with the formation of chloroform, carbon dioxide, and quinoline.

From pyridine and dichloroacetic acid are obtained the *salt*, which forms large crystals melting at 53°, but the base and the acid, when heated together, yield the basic hydrochloride of pyridinebetaine (m. p. 167°) described by Krüger (Abstr., 1891, 941, 1388), who gives the melting point as 159°. Quinoline and dichloroacetic acid yield the *dichloroacetate*, which forms white crystals melting at 63—64°; if the base and acid are heated together at 100°, quinolinemethylene chloride

is obtained and isolated in the form of a platinichloride, which crystallised with $2H_2O$; Rhoussopoulos (*loc. cit.*) prepared this compound and described an anhydrous platinichloride. When heated with excess of dichloroacetic acid, quinoline hydrochloride is the only crystalline product isolated.

With chloroacetic acid, pyridine yields a betaine (Vongerichten, Abstr., 1882, 1109), but quinoline gives a basic *salt* of a betaine, $C_9NH_7(OH)\cdot CO_2H,C_9NH_7<^{-O-}_{CH_2}>CO,HCl$, melting at 156°.

No simple reaction takes place in the case of quinoline and ethyl trichloroacetate; quinoline hydrochloride was the only crystalline product isolated.

Dimethylaniline does not yield salts with either of the three chloroacetic acids; with mono- and di-chloroacetic acids, the hydrochloride of the betaine originally prepared by Zimmermann (Abstr., 1880, 162) is alone formed; with trichloroacetic acid, profound decomposition takes place.

Strychnine and chloroacetic acid readily give the betaine prepared by Strecker (*Ber.*, 1871, 4, 821); with dichloroacetic acid, only a *salt* is produced, which forms white crystals melting at 120—122°.

K. J. P. O.

Synthesis of 2:6-Disubstituted Pyridines. Constitution of Pyridine. MAX SCHOLTZ and A. WIEDEMANN (*Ber.*, 1903, **36**, 845—854. Compare Abstr., 1895, i, 563; 1899, i, 717).—In order to demonstrate the identity of the positions 2 and 6 in the pyridine nucleus, the oximes of the two ketones, tolyl δ-phenylbutadiene ketone, $CHPh:CH\cdot CH:CH\cdot C(:NOH)\cdot C_7H_7$, and phenyl δ-tolylbutadiene ketone, $C_7H_7\cdot CH:CH\cdot CH:CH\cdot C(:NOH)Ph$, have been respectively converted into 2-phenyl-6-tolylpyridine; the same base was obtained from each ketone, and thus the identity of the positions 2 and 6 experimentally proven.

p-*Tolyl δ-phenylbutadiene ketone*, $CHPh:CH\cdot CH:CH\cdot CO\cdot C_6H_4Me$, is prepared from *p*-tolyl methyl ketone and cinnamaldehyde, which readily condense in the presence of dilute sodium hydroxide in alcoholic solution; the ketone crystallises in yellow leaflets melting at 89°, and gives with sulphuric acid a deep red coloration; the *oxime* crystallises in colourless scales melting at 170°. 2-*Phenyl*-6-*tolylpyridine* is obtained when the oxime is submitted to dry distillation; it crystallises in leaflets melting at 89° and yields a *picrate* which crystallises in slender needles melting at 163°; the *platinichloride* crystallises with $2H_2O$ in pale red needles melting at 184°; the *aurichloride* crystallises in yellow needles melting at 183°; the *mercurichloride* is a curdy precipitate decomposed by water.

On reducing the phenyltolylpyridine, a mixture of two inactive phenyltolylpiperidines is produced; these are separated by fractional crystallisation of the hydrochlorides, the one *hydrochloride* being sparingly soluble and melting at 283—284°, the other being soluble and melting at 222—223°; from the hydrochloride with the higher melting point, a *base* is obtained which crystallises in needles, melting

at 41·5° and boiling at 237—239° under 44 mm. pressure; the *picrate* melts at 183—184° and the *aurichloride* at 211—212°; the *platinichloride* crystallises with $2H_2O$, darkens very considerably at 200°, and melts and decomposes at 208—209°; the *hydrobromide* forms colourless prisms melting at 270°, the *hydriodide*, long needles melting at 250°; the *sulphate* forms crystalline aggregates melting and decomposing at 249°. iso-2-*Phenyl*-6-*tolylpiperidine*, prepared from the hydrochloride with the lower melting point, is an oil boiling at 218—220° under 20 mm. pressure; the *picrate* crystallises in yellow needles melting at 175—176°, the *aurichloride* in golden-yellow needles which become dark at 180° and melt and decompose at 199°; the *platinichloride* crystallises with $2H_2O$ and becomes dark at 180° and melts at 190°; the *hydrobromide* is readily soluble and melts at 267°; the *hydriodide* is very readily soluble and unstable, the crystals soon becoming yellow; it darkens at 185° and melts above 200°; the *sulphate* was only obtained as an oil.

p-*Methylcinnamaldehyde*, $C_6H_3Me\cdot CH\colon CH\cdot CHO$, was prepared by condensing *p*-tolualdehyde with acetaldehyde in the presence of sodium hydroxide, the reaction being complete in 24 hours at 25—30°; the product is acidified and the aldehyde extracted with ether and then distilled under reduced pressure; the aldehyde crystallises in yellow leaflets melting at 41·5° and boiling at 154—159° under 25 mm. pressure; the *phenylhydrazone* crystallises in yellow needles melting at 145°, the *semicarbazone* in colourless needles melting at 210°, and the *oxime* in leaflets melting at 135—136°.

Phenyl δ-p-*tolylbutadiene ketone*, $C_7H_7\cdot CH\colon CH\cdot CH\colon CH\cdot COPh$, prepared by condensing *p*-methylcinnamaldehyde and acetophenone under the influence of dilute sodium hydroxide, forms yellow leaflets melting at 100°; the *oxime* crystallises in white needles melting at 128—129°; when distilled, it is converted into 2-*p*-tolyl-6-phenylpyridine, which has been described above.

In order to synthesise 2 : 6-ditolylpyridine, *p*-methylcinnamaldehyde was condensed with methyl *p*-tolyl ketone in the presence of dilute alkali; p-*tolyl* δ-p-*tolylbutadiene ketone*,

$$C_6H_4Me\cdot CH\colon CH\cdot CH\colon CH\cdot CO\cdot C_6H_4Me,$$

thus formed, crystallises in yellow needles melting at 123—124°; its *oxime* crystallises in leaflets melting at 178°. 2 : 6-*Di*-p-*tolylpyridine*, prepared from the oxime, crystallises in leaflets melting at 162°; the *picrate* forms yellow needles melting at 174°, the *aurichloride*, yellow leaflets melting at 211—212°.

p-*Methoxycinnamaldehyde*, $OMe\cdot C_6H_4\cdot CH\colon CH\cdot CHO$, was obtained in small yield by condensing anisaldehyde with acetaldehyde, and crystallised in yellow needles melting at 58° and boiling at 173—176° under 14 mm. pressure; the *phenylhydrazone* melts at 136—137°, the *semicarbazone*, which crystallises in colourless needles, at 199°. With acetophenone, the aldehyde condenses in the presence of dilute sodium hydroxide, yielding *phenyl* δ-p-*methoxyphenylbutadiene ketone*,

$$OMe\cdot C_6H_4\cdot CH\colon CH\cdot CH\colon CH\cdot COPh,$$

which forms yellow crystals melting at 118°. K. J. P. O.

4-Benzyl*iso*quinoline. LEOPOLD RÜGHEIMER and B. FRILING (*Annalen*, 1903, 326, 261—284).—This paper is the first of a series which contains an account of the benzyl*iso*quinolines, in which the benzyl group replaces a hydrogen atom in the pyridine nucleus; three such compounds are possible according as the benzyl group is attached to the carbon atoms in the 1-, the 3-, or the 4-position, and their preparation has been previously briefly recorded (Abstr., 1900, i, 522).

4-Benzyl*iso*quinoline is formed together with a much smaller quantity of the 3-isomeride when benzoyltetrahydro*iso*quinoline is heated with benzaldehyde under pressure for 6 hours at 200°, a method originally used in synthesising benzylpyridines (Abstr., 1894, i, 549), and is separated from the isomeride by first washing the crystals with ether and then recrystallising from alcohol; it crystallises in plates belonging to the monoclinic system [$a:b:c = 1{\cdot}3934:1:0{\cdot}7833$; $\beta = 103°49'$], melts at 117·5—118°, boils at 238° under 23 mm. pressure, and is volatile with steam. It is a feeble base; the *hydrochloride* crystallises in slender needles; the *platinichloride* in pale reddish-yellow leaflets melting at 219—220°; the *mercurichloride*, $(C_{16}H_{13}N,HCl)_2,HgCl_2,\frac{1}{2}H_2O$, crystallises in needles, and, when anhydrous, melts at 165—166°; the *nitrate* crystallises in needles, and the *sulphate* in prisms melting at 208—209°; the *picrate*, which is characteristic of this benzyl*iso*quinoline, crystallises in long, yellow needles melting at 190—191°. The base, in suspension in water, was oxidised with 3 per cent. potassium permanganate; from the product of oxidation, pyridine-3:4:5-tricarboxylic acid (decomposing at 261°; compare Weber, Abstr., 1887, 1117) was isolated and analysed in the form of its silver salt.

4-p-*Nitrobenzyl*iso*quinoline*, $C_9NH_6{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, prepared by adding the base in small portions at a time to a mixture of nitric and acetic acids, crystallises in needles melting at 128·5—129°, and is oxidised by chromic acid in acetic acid solution to *p*-nitrobenzoic acid (m. p. 237—238°); the *nitrate* forms yellow plates melting at 184—185°. On reduction with stannous chloride, an insoluble tin double salt is formed, from which 4-p-*aminobenzyl*iso*quinoline* is obtained, crystallising in colourless needles melting at 160—161°; the compound is dibasic and forms a *platinichloride*, $NH_2{\cdot}C_{16}H_{12}N,H_2PtCl_6,4H_2O$, which crystallises in yellow needles; when anhydrous, the salt loses its colour at 240°, but is not molten at 260°. The *acetyl* derivative crystallises in small needles melting at 181—182°, and on treatment with fuming nitric acid yields 4-m-*nitro*-p-*acetylaminobenzyl*iso*quinoline*,

$$C_9NH_6{\cdot}CH_2{\cdot}C_6H_3(NO_2){\cdot}NHAc,3H_2O,$$

which crystallises in yellow needles, melting at 144—145° when anhydrous; the *nitrate* of this base forms needles melting at 200—201°; on hydrolysis, the acetyl derivative is converted into 4-m-*nitro*-p-*amino-benzyl*iso*quinoline*, which crystallises in small, red needles melting at 231—232°. When reduced with stannous chloride in the presence of alcohol, it is converted into an *o*-diamine, as is shown by the fact that with ammonium thiocyanate a thiocarbamide of the type

$$C_xH_y{<}{NH \atop NH}{>}CS$$

is formed. Such thiocarbamides, which can only be obtained from *o*-diamines, do not lose sulphur when treated with an alkaline solution

of lead, and thus can be readily distinguished from other thiocarbamides.

When the nitrate of *p*-nitrobenzyl*iso*quinoline is added to sulphuric acid, a *dinitro*-derivative is formed, which crystallises in needles melting at 149—150°. K. J. P. O.

Derivatives of 4-Benzyl*iso*quinoline. LEOPOLD RÜGHEIMER and E. ALBRECHT (*Annalen*, 1903, **326**, 285—294).—Dinitrobenzyl*iso*quinoline (m. p. 149—150°; preceding abstract) can be oxidised by 5 per cent. permanganate when suspended in water; from the products of oxidation, *p*-nitrobenzoic acid can be easily isolated, and at the same time a very small quantity of a nitrophthalic acid, which is certainly not the 1 : 2 : 4-acid, and is very probably the 1 : 2 : 3-acid. The second nitro-group therefore enters the benzene nucleus of the *iso*quinoline complex.

4-p-*Hydroxybenzyl*iso*quinoline*, $C_9NH_6·CH_2·C_6H_4·OH$, could only be prepared from the corresponding *p*-aminobenzyl*iso*quinoline by making the solid diazonium chloride, which was obtained in colourless, crystalline aggregates, and then boiling its aqueous solution; the phenol crystallised in yellow leaflets from amyl alcohol, which become coloured at 233°, melts at 238°, and gives a pale orange coloration with ferric chloride. The *platinichloride* crystallises in microscopic, yellow needles with $2H_2O$, and begins to decompose at 140° when anhydrous. 4-p-*Methoxybenzyl*iso*quinoline*, prepared by heating the solution of the diazonium compound in methyl alcohol under pressure at 100°, could only be obtained as an oil, which was converted into a *platinichloride*. On boiling the alcoholic solution of the diazonium salt with reduced copper, the diazo-group is replaced by hydrogen, 4-benzyl*iso*quinoline being formed. K. J. P. O.

Derivatives of 4-Benzyl*iso*quinoline. LEOPOLD RÜGHEIMER and L. SCHAUMANN (*Annalen*, 1903, **326**, 295—296).—4-*Benzyl*iso*quinoline methiodide* is readily prepared by the direct union of its constituents, and crystallises in needles melting at 188°; the corresponding *ethiodide* crystallises in leaflets which melt and become red at 188—189°.

On heating 4-*p*-hydroxybenzyl*iso*quinoline with methyl iodide and potassium hydroxide in the presence of methyl alcohol under pressure at 100°, 4-p-*methoxybenzyl*iso*quinoline methiodide* is obtained, and crystallises from water in yellow needles melting and decomposing at 219°. K. J. P. O.

Some Homologues of 4-Benzyl*iso*quinoline. LEOPOLD RÜGHEIMER and E. ALBRECHT (*Annalen*, 1903, **326**, 297—304. Compare preceding abstracts).—On heating benzoyltetrahydro*iso*quinoline (1 mol.) with *p*-tolualdehyde ($1\frac{1}{2}$ mols.) under pressure for six hours at 200°, 4-p-*methylbenzyl*iso*quinoline*, $C_9NH_6·CH_2·C_6H_4Me$, is formed and can be purified by conversion into the sulphate, which is crystallised from alcohol; the base crystallises in long needles melting at 66—67°; the *sulphate* crystallises in small needles melting at

209—210°; the *platinichloride* crystallises with H_2O and when anhydrous begins to decompose at 203°; the *mercurichloride*,

$$(C_{17}H_{15}N,HCl)_3,2HgCl_2,$$

crystallises in needles melting at 160·5—162°; the *picrate* crystallises in slender plates or yellow needles melting at 196—197°.

4-p-iso*Propylbenzyl*iso*quinoline* (4-*cuminyl*iso*quinoline*),

$$C_9NH_6\cdot CH_2\cdot C_6H_4Pr^\beta,$$

prepared from benzoyltetrahydro*iso*quinoline and cuminaldehyde, can be purified by conversion into the hydrochloride, which is recrystallised from benzene; the base crystallises in large prisms melting at 72·5—73·5°; the *hydrochloride*, prepared by passing hydrogen chloride into a benzene solution of the impure base, crystallises in microscopic leaflets; the *platinichloride* is crystalline and anhydrous and begins to decompose at 213°; the *mercurichloride*,

$$C_9NH_6\cdot CH_2\cdot C_6H_4Pr^\beta,HCl,HgCl_2,$$

crystallises in needles melting at 197—198°; the *picrate* forms yellow needles melting at 176°. K. J. P. O.

Formation of Flavaniline. Carl Goldschmidt (*Chem. Zeit.*, 1903, 27, 279).—When acetophenoneoxime is heated at 60° with excess of phosphoric oxide, flavaniline (m. p. 97°) is formed and can be extracted from the product with ether after neutralisation. The oxime has probably been transformed into acetanilide (Beckmann's transformation), which has then condensed to 2-*p*-aminophenyl-4-methylquinoline (flavaniline) (compare O. Fischer, Abstr., 1882, 1066, and 1883, 600.)

The formation of *iso*quinoline from the oxime of cinnamaldehyde, the oxime of benzylideneacetone, and the oxime of dibenzylidene under the influence of phosphoric acid is probably the result of a similar series of changes. The oxime of benzylideneacetone is first converted into acetophenylvinylamine, CHPh:CH·NHAc, which then condenses with loss of water to *iso*quinoline. It is intended to pursue the investigation of the latter change. K. J. P. O.

Characterisation of Cyclic Ketones. Pavel Iw. Petrenko-Kritschenko and E. Eltschaninoff (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 146—155. Compare Abstr., 1901, i, 506; and Petrenko-Kritschenko and Lordkipanidze, Abstr., 1901, i, 505).—In studying the course of the reaction between a ketone and phenylhydrazine in alcoholic solution, it is very necessary that the alcohol should be freed from traces of aldehyde and other impurities and, even when this has been done to as great an extent as possible, one and the same sample of alcohol should always be used in comparative experiments.

After showing that this reaction is practically irreversible, the authors determined the amount of change taking place when a ketone and phenylhydrazine, the concentration of each being $N/100$, are allowed to react together in 50 per cent. alcoholic solution for one hour at 25°, the following being the results obtained in percentages of the total change possible. Except where otherwise stated, 1 mol. of the ketone was present for every mol. of the phenylhydrazine:

Acetone	51	Acetonylacetone (1 mol.)	20·7
Methyl ethyl ketone	38·1	Acetonylacetone ($\frac{1}{2}$ mol.)	16·2
Methyl propyl ketone	27	Suberone	26·3
Methyl hexyl ketone	25·7	Ketohexamethylene	32·3
Methyl *sec.*-propyl ketone	15·6	Diketohexamethylene ($\frac{1}{2}$ mol.)	43·3
Methyl *ter.*-butyl ketone	3·6	Ketopentamethylene	36·5
Diethyl ketone	12·4	Ethyl tetramethylene ketone	6·1
Ethyl propyl ketone	10	Methyltrimethylene ketone	5·6
Dipropyl ketone	7·5		
Methyl dimethylallenyl ketone	3·6		

Comparing the results for the following pairs of compounds: suberone and dipropyl ketone; ketohexamethylene and ethyl propyl ketone; diketohexamethylene and acetonylacetone; ketopentamethylene and diethyl ketone, it is seen that the velocity of reaction of the cyclic ketones with phenylhydrazine is greater than that of the corresponding fatty ketones. Further, the capacity for reaction is greater for a four-membered ring than for one containing 3 atoms, whilst for rings of 5, 6, 7, and 8 atoms a continuous fall takes place.

The results are discussed in the light both of the views previously advanced by Petrenko-Kritschenko (*loc. cit.*) and of Baeyer's theory concerning the varying stability of ring compounds. T. H. P.

Action of Phenylhydrazine on Formic Esters. L. Baidakowsky and Sergius N. Reformatsky (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 61—67).—The interaction of molecular proportions of phenylhydrazine and ethyl formate yields formylphenylhydrazine, NHPh·NH·CHO, and on treating this with another molecule of phenylhydrazine and distilling, the following products are obtained: water, benzene, aniline, phenylcarbylamine, unaltered phenylhydrazine, diphenyltetrazoline, ammonia, carbon monoxide, nitrogen, and a crystalline *compound* melting at 126°. The reaction is represented by the equation: $7NHPh{\cdot}NH{\cdot}CHO = 5H_2O + C_6H_6 + NH_2Ph + 3Ph{\cdot}NC + C_{14}H_{12}N_4 + 2N_2 + 2NH_3 + 2CO$. T. H. P.

Action of Phenylhydrazine on Benzoic, Acetic, and *iso*Valeric Esters. L. Baidakowsky and I. Slepaka (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 68—71).—The formation of benzoyl-, acetyl-, and *iso*valeryl-phenylhydrazines by the action of phenylhydrazine on ethyl benzoate, acetate, or *iso*valerate takes place with difficulty, and only small yields are obtained (compare preceding abstract).

In the case of phenylhydrazine and ethyl benzoate, if the heating is prolonged or is carried out in a sealed tube, benzoylanilide, benzamide, nitrogen, and ammonia are formed.

Acetylphenylhydrazine, NHPh·NHAc, melts at 128—129°, and *iso-valerylphenylhydrazine*, $NHPh{\cdot}NH{\cdot}COC_4H_9$, at 141°. T. H. P.

Interaction of Zinc Ethyl and Benzenediazonium Chloride. M. M. Tichwinsky (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 155—170).—The interaction of zinc ethyl and benzenediazonium chloride in

ether gives rise to ethyl chloride, benzidine, *sym.*-diethylbenzidine, phenylethylhydrazine, and phenyldiethylhydrazine.

Diethylbenzidinedinitrosoamine, $C_{12}H_8(N·NO·Et)_2$, crystallises from alcohol in pale yellow needles or plates, melts at 163°, and is soluble in light petroleum; it gives Liebermann's reaction.

Diacetyldiethylbenzidine, $C_{12}H_8(NEtAc)_2$, crystallises in thick, colourless prisms, melts at 167° and dissolves readily in benzene.

Dibenzoyldiethylbenzidine is deposited from aqueous alcohol in silky needles, melts at 185°, and dissolves readily in benzene or ether, and to a slight extent in light petroleum.

Phenyldiethylhydrazine, NEtPh·NHEt, is a colourless, mobile oil, having a pleasant, aromatic odour and boiling at 111—115° under 12 mm. pressure; it is readily soluble in the organic solvents, but only slightly so in water. The *benzoyl* derivative, NEtPh·NEtBz, crystallises from light petroleum in colourless, well-formed, thick rhombohedra melting at 60°. The *nitrosoamine*, NEtPh·NEt·NO, is a yellow oil which is insoluble in water and gives Liebermann's reaction.

Phenylethylhydrazine was obtained as its *benzoyl* derivative

NEtPh·NHBz,

which crystallises in long, thin needles melting at 168° and dissolves slightly in benzene, alcohol, or ether. T. H. P.

Formation of Rings. RICHARD MEYER (*Annalen*, 1903, 327, 1—58).—In a *résumé* of our present knowledge of the formation of closed rings from open chains, the author draws attention to the exceptional fact that carbamides and thiocarbamides of the types $C_6H_4<^{NH}_{NH}>CO$, and $C_6H_4<^{NH}_{NH}>CS$ are formed not only from aromatic *o*-diamines, but also from *m*- and *p*-diamines, whereas similar derivatives of oxalic acid and diamines have only been obtained from the *o*-compound, the *m*- and *p*-diamines giving compounds of the type $C_6H_4(NH·CO·CO_2Et)_2$. Recently, such rings, which, however, contain sulphur, have been prepared from *o*-, *m*-, and *p*-xylene (Kötz and Sevin, Abstr., 1900, i, 343; and Autenrieth and Hennings, Abstr., 1902, i, 389). With the object of throwing further light on this subject, a study has been made of the interaction of the acids, malonic, succinic, *iso*succinic, adipic, sebacic, and phthalic, with *o*-, *m*-, and *p*-diamines.

[With JOH. MAIER.]—When concentrated alcoholic solutions of either of the three phenylenediamines and succinic acid are mixed and evaporated, the succinate, $NH_2·C_6H_4·NH_2,CO_2H·C_2H_4·CO_2H$, is obtained; it is crystalline and stable in the absence of moisture, but when heated decomposes, yielding the substances mentioned below.

When *o*-phenylenediamine is heated with succinic acid at 150—180°, three substances are formed: *o*-phenylenesuccinamide,

$$C_6H_4<^{NH·CO}_{NH·CO}>C_2H_4,$$

having an eight-membered ring, the *base*, $C_2H_4(CO·NH·C_6H_4·NH_2)_2$, and the acid *amidine*, $C_6H_4<^{N}_{NH}>C·C_2H_4·CO_2H$, which always forms the main product of the reaction. From the product obtained by

heating mol. proportions of *o*-phenylenediamine hydrochloride, succinic acid, and anhydrous sodium carbonate together at 150—180°, the amide first mentioned is extracted with alcohol; it melts at 236°, has an intensely sweet taste, and both acid and basic properties (compare Anderlini, Abstr., 1894, i, 375); from the residue, the base is extracted in the form of its hydrochloride by water; the hydrochloride crystallises in very long needles which contain water; from it, the base is obtained in microscopic needles which melt above the temperature attainable by use of a sulphuric acid bath. From the mother liquor, from which the base has been separated by means of ammonia, the acid amidine is obtained on concentrating; it crystallises from water in pale yellow prisms melting at 226°, and has both acid and basic properties; the *ester* can be prepared by saturating its suspension in alcohol with hydrogen chloride; it crystallises in long needles and is converted into an *amide* by ammonia.

m-Phenylenediamine and succinic acid yield the *m*-phenylenedisuccinimide described by Biedermann (this Journal, 1877, i, 474; ii, 783).

From the product of the interaction of *p*-phenylenediamine and succinic acid, p-*aminosuccinanil*, $NH_2\cdot C_6H_4\cdot N<^{CO}_{CO}>C_2H_4$, is extracted from the product of the reaction by alcohol, and crystallises in needles melting at 236°; from the residue, insoluble in alcohol, left after the extraction of the base just described, p-*phenylenedisuccinimide*, $C_6H_4\left(N<^{CO}_{CO}>C_2H_4\right)_2$, can be extracted by acetic acid; it crystallises in rhombic plates and can be sublimed in long needles, the melting point of which lies very high; it can be distinguished from the corresponding *m*-derivative by the fact that it is easily nitrated by nitric acid, whilst the *m*-compound can be crystallised from the boiling acid without change.

Both malonic acid and *iso*succinic acid give the corresponding amides when heated with *o*-phenylenediamine.

o-, *m*-, and *p*-Phenylenediamines readily react with succinic anhydride in alcoholic solution; the *o*-compound yields *o*-phenylenesuccinamide, whilst the *m*- and *p*-compounds give disuccinamic acids. The *acid* prepared from *m*-phenylenediamine, $C_6H_4(NH\cdot CO\cdot C_2H_4\cdot CO_2H)_2$, forms colourless needles which sinter at 180°, melt at 215°, and decompose at 220—221°; it is readily hydrolysed when heated with water at 100°, especially if a trace of acid is present, and with acetic anhydride gives diacetyl-*m*-phenylenediamine. p-*Phenylenedisuccinamic acid*, prepared from succinic anhydride and *p*-phenylenediamine, crystallises in lustrous needles melting at 262°; when heated a few degrees above its melting point, it again solidifies and sublimes at a higher temperature; under the influence of heat, it is converted into a mixture of *p*-phenylenedisuccinimide and *p*-aminosuccinanil, which can be separated into its components by acetone, the latter compound alone being soluble.

o-Phenylenediamines and the anhydrides of dicarboxylic acids were found by Anderlini (*loc. cit.*), when mixed in such solvents as benzene, which do not contain a hydroxyl group, to give additive products, which easily passed into phenylenediamides. *o*-Phenylenediamine and succinic anhydride in solution in ethyl acetate yield an oil which rapidly passes

into *o*-phenylenesuccinamide when heated with alcohol or acetone. *m*-Phenylenediamine and succinic anhydride yield a *solid* substance crystallising in soluble needles melting at 156—166°, and changes rapidly, even when kept at the ordinary temperature, into *m*-phenylenedisuccinamic acid (m. p. 215°). The *additive* product, prepared from *p*-phenylenediamine, melts at 183° and changes, when heated or when kept, into *p*-phenylenedisuccinamic acid. When this additive product is heated to a high temperature, the disuccinamic acid first formed decomposes in its usual manner, giving *p*-phenylenedisuccinimide and *p*-aminosuccinanil. These additive products are thought to be represented not by the formula $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_2H_4 \cdot CO_2H$, but by the expression $NH_2 \cdot C_6H_4 \cdot NH \cdot C(OH) < \begin{smallmatrix} C_2H_4 \\ O \end{smallmatrix} > CO$, as this more truly expresses their great instability.

Phthalic anhydride and *o*-phenylenediamine react in alcoholic solution forming *o*-phenylenephthalamide (m. p. 277°; compare Anderlini, *loc. cit.*) and o-*phenylenediphthalimide*, $C_6H_4\left(N < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_4\right)_2$, which is insoluble in alcohol and can therefore be easily separated from the soluble phthalimide; it melts at 292°. Phthalic anhydride and *m*-phenylenediamine yield two substances, the di-imide, and *m*-aminophthanil, $NH_2 \cdot C_6H_4 \cdot N < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_4$ (brass-yellow needles melting at 190°), which was prepared by Biedermann (*loc. cit.*), and thought by him to be the diamide; but it has basic properties, can be diazotised, and has been prepared from *m*-nitrophthalanil (compare Geigy & Co., D.R.-P. 126964, 1900). From *p*-phenylenediamine and phthalic anhydride, *p*-aminophthalanil, $NH_2 \cdot C_6H_4 \cdot N < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_4$, was obtained in pale yellow needles melting at 250° (compare Biedermann, who gives the melting point at 182°).

When *m*- or *p*-phenylenediamine and phthalic anhydride are mixed in ethyl acetate solution, very unstable additive compounds are formed; the m-*derivative* melts at 151°, and then again solidifies as it changes into *m*-aminophthalanil and *m*-phenylenediphthalimide; the p-*derivative* has no sharp melting point, but changes when heated into a mixture of *p*-phenylenediphthalimide, which can be extracted with acetone and melts at 356°, and *p*-aminophthalanil (yellow needles), which remains behind in the acetone mother liquor.

In order to fix the constitution of the amino anils described above, these compounds have been prepared from the nitro-anils. *o*-Nitrosuccinanil is prepared by melting together *o*-nitroaniline and succinic acid, and is reduced by adding reduced iron and a little acetic acid to its hot alcoholic solution (by tin and hydrochloric acid, it is both reduced and hydrolysed); o-*aminosuccinanil* crystallises in snow-white needles melting and decomposing at 230—232°, and is readily diazotised. m-*Nitrosuccinanil* is prepared in the same manner as the *o*-compound, crystallises in colourless prisms melting at 175—176°, and is reduced by iron and acetic acid in acetone solution to m-*aminosuccinanil*, which forms pale yellow crystals melting at 196—198°.

In a similar manner, *p*-aminosuccinanil is obtained from *p*-nitrosuccinanil.

o-*Aminophthalanil* is prepared by reducing with iron and acetic acid the corresponding nitro-derivative suspended in dilute alcohol, and crystallises in slender yellow needles melting at 184—186°. The *m*- and *p*-aminophthalanils were prepared in a similar manner from the corresponding nitro-derivatives.

In the course of attempts, which were unsuccessful, to prepare aminoanilic acids of the type $NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot R''\cdot CO_2H$, a series of nitroanilic acids have been obtained. These substances were all prepared by dissolving mol. proportions of the nitroaniline and the acid anhydride in ethyl acetate, and then evaporating the solvent, when the additive product is left in a crystalline form. o-*Nitrosuccinanilic acid*, $NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot C_2H_4\cdot CO_2H$, forms pale yellow crystals melting at 131°, and is very readily hydrolysed by water; the m-*nitro*-derivative crystallises in colourless leaflets melting at 181—182°; the *sodium* salt crystallises in needles, the p-*nitro*-compound forms pale yellow needles melting at 202°. o-*Nitrophthalanilic acid* crystallises in yellow leaflets melting at 145—146°, the m-*nitro*-compound in yellow needles melting at 240°, and the p-*nitro*-derivative in pale yellow needles or plates which melt with evolution of gas at 190—192°, and then solidify, to melt again at 260°. The rate at which these nitro-compounds were hydrolysed by boiling water was measured, using a colorimetric method.

K. J. P. O.

Quinazoline. Siegmund Gabriel (*Ber.*, 1903, 36, 800—813).—2-*Mercaptoquinazoline*, $C_6H_4<\begin{matrix}CH{:}N\\ N{=}C\cdot SH\end{matrix}$, prepared by the action of potassium hydrosulphide on the chloro-compound, crystallises from boiling alcohol in hexagonal plates, sinters at 225°, melts at 229—231° to a reddish-brown liquid, and dissolves in alkalis, but is reprecipitated by boiling with ammonium chloride.

Unsuccessful attempts were made to prepare quinazoline by condensing *o*-aminobenzaldehyde with formamide, and then with the formamideoxime, $NH_2\cdot CH{:}NOH$. Similarly, the action of formamide on *o*-aminobenzaldoxime gave *o*-aminobenzonitrile, but not quinazoline. By diazotising and reducing *o*-aminobenzonitrile, o-*cyanophenylhydrazine*, $CN\cdot C_6H_4\cdot NH\cdot NH_2$, was prepared; this crystallises from benzene in silvery scales, melts at 152—153°, and is identical with the base which Pinnow and Sämann prepared (Abstr., 1896, i, 366) from ketodihydrophenotriazinoxime and formulated as a phenotriazine derivative; the *hydrochloride* melts at 160—161°, the *sulphate* at 215—218°, the *acetyl* derivative at 182—183°, the *benzoyl* derivative at 177—178°, whilst the picrate decomposed at about 238° (Pinnow and Sämann gave 169°, 225°, 182°, 179°, and 241° respectively).

Dihydroquinazoline, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ N=CH\end{matrix}$, which can be prepared in good yield from *o*-formaminobenzylamine by a slightly modified method, distils, with slight decomposition, at 303—304° under 769 mm. pressure,

crystallises from water in colourless needles, and dissolves in 40 parts of water at 16°. By oxidising this base with potassium ferricyanide, *quinazoline*, $C_6H_4<\begin{matrix}CH{:}N\\ N{=}CH\end{matrix}$, was at last successfully prepared; it boils at 243° under 772·5 mm. pressure, melts at 48—48·5°, has a normal molecular weight when dissolved in diphenyl, dissolves easily in water to a neutral solution, from which it is precipitated by potassium hydroxide, crystallises from light petroleum in glistening flakes resembling naphthalene, has a bitter, burning taste, and, unlike its homologues, which have an odour of acetamide, it is odourless at the ordinary temperature, and, when warmed, emits an odour suggesting that of quinoline or phthalazine. The *hydrochloride* and *sulphate* are very soluble; the *nitrate* crystallises in microscopic plates; the *picrate* is precipitated in minute needles and melts at 188—190°; the *mercurichloride* forms minute, white crystals, and the *ferricyanide* forms minute flakes; the *platinichloride*, $C_8H_6N_2,H_2PtCl_6$, forms flat, pointed, orange-yellow prisms and melts at 250°; the *aurichloride*, $C_8H_6N_2,HAuCl_4,H_2O$, forms orange-red, rhombohedral crystals and melts at 185°.

2-Methylquinazoline, $C_6H_4<\begin{matrix}CH{:}N\\ N{=}CMe\end{matrix}$, prepared by a similar method, crystallises from light petroleum in pale yellow, flat needles, sinters at 40°, melts at 41—42°, and is identical with the base described by Bischler and Lang (Abstr., 1891, 745).

Tetrahydroquinazoline, $C_6H_4<\begin{matrix}CH_2{\cdot}NH\\ NH{-}CH_2\end{matrix}$ (Busch, Abstr., 1894, i, 1148; 1895, i, 306), prepared by reducing dihydroquinazoline, crystallises from water in flat, pointed, rhombic forms as a *hydrate*, $C_8H_{10}N_2,H_2O$, which melts at 49—51°; the *anhydrous* base crystallises from light petroleum in pointed needles and melts at 76°; the hydrochloride crystallises in flat needles and melts at 193—195° (Busch, 192°); the platinichloride forms orange-yellow scales.

2-*Methyltetrahydroquinazoline*, $C_6H_4<\begin{matrix}CH_2{\cdot}NH\\ NH{-}CHMe\end{matrix}$, prepared by a similar method, does not form a crystalline hydrate, has an odour similar to that of benzonitrile, has a bitter taste, and dissolves in water to a strongly alkaline solution. The *picrate* forms long, flat, pointed needles, sinters at 175°, and melts at 179°. The *picrate* of the *dihydro*-base forms stout prisms, and sinters at 175° and melts at 185—187°. Hydrochloric acid converts the base into acetaldehyde and *o*-benzylenediamine. T. M. L.

Indanthrene. I. Felix Kaufler (*Ber.*, 1903, 36, 930—933).—The substance "A," of the German Patent 135407 (compare Abstr., 1902, i, 721), which is insoluble in nitrobenzene, can be purified by dissolving it in concentrated sulphuric acid and allowing the solution to gradually absorb water; well-formed, blue needles separate which, in the case of "Indanthrene C," have the composition $C_{28}H_{10}O_4N_2Br_2$, and, in the case of indanthrene itself, the composition $C_{28}H_{12}O_4N_2$. Both indanthrene and its brominated derivative give the same *substance*, $C_{28}H_{16}O_2N_2$, when heated with hydriodic acid of sp. gr. 1·96

for 4 hours at 250—280°; it sublimes, or crystallises from nitrobenzene, in beautiful, red needles, is non-basic, and probably has the structure $C_6H_4<\begin{matrix}CH_2\cdot C\text{————}C\cdot N\cdot C\cdot CH\cdot CH\cdot C—CO\\ CO—C\cdot CH:CH\cdot C\cdot N\cdot C\text{————}C\cdot CH_2\end{matrix}>C_6H_4$, whilst indanthrene is probably the corresponding anthraquinoneazine,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}N\\N\end{matrix}>C_6H_2<\begin{matrix}CO\\CO\end{matrix}>C_6H_4.$$

W. A. D.

Diaminophenylphenonaphthacridine. FRITZ ULLMANN and E. GRETHER (*Zeit. Farb. Text. Chem.*, 1903, 2, 89—92).—*p*-Acetylaminobenzaldehyde is best prepared by heating commercial *p*-anhydroaminobenzaldehyde with a mixture of water, glacial acetic acid, acetic anhydride, and sodium acetate; when heated with *m*-tolylenediamine and β-naphthol at 200°, 9-*amino*-12-p-*acetylaminophenyl*-10-*methylpheno*-*$\alpha\beta$-naphthacridine*, $NH_2\cdot C_6H_2Me<\begin{matrix}C(C_6H_4\cdot NHAc)\\N\text{—————}\end{matrix}>C_{10}H_6$, is obtained. It crystallises in yellow needles, melts at 313°, dissolves in boiling alcohol giving an orange-yellow solution with a greenish fluorescence, and forms a *hydrochloride* crystallising from alcohol in small, red leaflets; the *acetyl* derivative,

$$NHAc\cdot C_6H_2Me<\begin{matrix}C(C_6H_4\cdot NHAc)\\N\text{—————}\end{matrix}>C_{10}H_6,$$

obtained by acetylation, crystallises from nitrobenzene in colourless leaflets and melts at 354°.

9-*Amino*-12-p-*aminophenyl*-10-*methylpheno*-*$\alpha\beta$-naphthacridine*, obtained by hydrolysing the foregoing monoacetyl derivative with dilute sulphuric acid, separates from nitrobenzene on adding ether in small, yellow crystals and melts at 318°; the *dihydrochloride*, $C_{24}H_{21}N_3Cl_2$, crystallises from 80 per cent. acetic acid in red needles.

p-*Acetylaminophenyltetraminoditolylmethane*,
$NHAc\cdot C_6H_4\cdot CH[C_6H_2Me(NH_2)_2]_2$ $[CH : Me : (NH_2)_2 = 1 : 3 : 4 : 6]$, prepared by heating together *m*-tolylenediamine and *p*-acetylaminobenzaldehyde in alcoholic solution, separates from aniline in white crystals, melts at 205°, and when heated with β-naphthol at 180° is converted by loss of *m*-tolylenediamine into 9-amino-12-*p*-acetylaminophenyl-10-methylpheno-$\alpha\beta$-naphthacridine (*supra*) and the leuco-base derived from this.

p-*Nitrophenyltetraminoditolylmethane*, prepared by heating *m*-tolylenediamine with alcoholic *p*-nitrobenzaldehyde, separates from aniline in red crystals, melts at 265°, and is easily reduced by stannous chloride to p-*aminophenyltetraminoditolylmethane*; this also crystallises from aniline, and, when heated with β-naphthol at 200°, yields the 9-amino-12-*p*-aminophenyl-10-methylpheno $\alpha\beta$-naphthacridine previously described.

W. A. D.

Mechanism of Friedländer's Reaction for Converting Diazotates [Diazoxides] into Hydrocarbons. ALEXANDER EIBNER (*Ber.*, 1903, 36, 813—818).—In converting diazoxides into hydrocarbons by means of an alkaline solution of stannous chloride, it is probable that phenylhydrazine is an intermediate product. This view

was confirmed in two ways. Phenylhydrazine (6 grams) and diazobenzene (from 5 grams of aniline) were found to yield benzene (5—6 grams), azobenzene and diazoaminobenzene being also formed, as in Friedländer's reaction. Again, considerable quantities of phenylhydrazine were actually isolated when the diazoxide was added to the stannous solution, the latter being covered with a layer of ether.

T. M. L.

Esters of Azo- and Azoxy-benzoic Acids. By FELIX MEYER and K. DAHLEM (*Annalen*, 1903, **326**, 331—346).—Using Vorländer and Meyer's method (Abstr., 1902, i, 328) of converting diazonium salts into azo-compound by means of ammoniacal cuprous oxide, a series of esters of azo- and azoxy-benzoic acids have been prepared.

Ethyl *p*-azobenzoate, previously prepared by the use of ammoniacal cuprous oxide, has now been obtained by oxidising ethyl *p*-aminobenzoate with chromic acid in acetic acid solution; it melts at 145·5° (corr.). *Ethyl* p-*hydrazobenzoate*, prepared by reducing the azo-compound with zinc and ammonia, crystallises in colourless needles melting at 118°, and is very readily oxidised by the air to the original azobenzoate, which now melts at 143°. The melting point, 114·5°, given in *Beilstein* (iv, 1459) and observed by Uspensky, is therefore incorrect. Uspensky obtained this ester by reducing ethyl *p*-nitrobenzoate in alcoholic solution with sodium amalgam; on repeating this preparation, a mixture of two coloured substances was obtained, which melted at 113—115° and could not be separated by crystallisation. As ethyl *p*-azoxybenzoate, which was prepared from the silver salt of *p*-azoxybenzoic acid, obtained by reducing *p*-nitrobenzoic acid with sodium arsenite, melts at 114·5° (corr.) to a turbid liquid, only becoming clear at 122·5°, it seemed probable that Uspensky's ethyl azobenzoate was a mixture of the ethyl esters of azo- and azoxy-benzoic acid. To decide this question, *p*-nitrobenzoic acid was reduced by sodium amalgam, and the acid obtained converted into silver salt; from the salt, the ester was prepared and found to melt at 113—115°. A mixture of the pure esters which was found to give the same melting point was not separable by crystallisation from alcohol.

Methyl *p*-azobenzoate, prepared by oxidising methyl *p*-aminobenzoate with chromic acid, crystallises in red needles melting at 242° (corr.); it was also prepared from the silver salt of *p*-azobenzoic acid. *Methyl* p-*azoxybenzoate*, prepared in the same manner as the corresponding ethyl ester, crystallises in yellow needles melting at 207° (corr.); on reducing methyl *p*-nitrobenzoate with sodium amalgam, or on treating the silver salt of the acids prepared by reducing *p*-nitrobenzoic acid with methyl iodide, a mixture of methyl azo- and azoxybenzoates is obtained melting at 202°, and not separable by crystallisation from alcohol.

Ethyl *m*-azobenzoate was prepared from *m*-nitrobenzoic acid, which was reduced to the hydrazo-acid by zinc dust or iron filings, and then oxidised by the air to the azo-acid, the silver salt of which was acted on by ethyl iodide; the ester resembled that prepared by the action of ammoniacal cuprous oxide on the diazonium salt (*loc. cit.*) and melted at 109° (corr.) (compare Golubeff and Fittica, *Beilstein*, iv,

1458). Ethyl *m*-azoxybenzoate was prepared from silver *m*-azoxybenzoate and ethyl iodide and melted at 78° (compare Uspensky, *loc. cit.*). *Methyl* m-*azobenzoate* crystallises in golden-yellow leaflets melting at 163° (corr.), and *methyl* m-*azoxybenzoate* in pale yellow leaflets melting at 134°.

Ethyl *o*-azobenzoate was prepared by reducing *o*-nitrobenzoic acid to *o*-azobenzoic acid (Griess, Abstr., 1878, 149), which was then converted into the ester by means of the silver salt; it crystallises in four-sided orange leaflets melting as 85°; Fittica's ester melted at 138—139° (Abstr., 1879, 152). *Ethyl* o-*azoxybenzoate* was prepared from *o*-nitrobenzoic acid, which was reduced by alcoholic potassium hydroxide to *o*-azoxybenzoic acid (Griess, this Journal, 1875, 460; and Uspensky, Abstr., 1893, i, 164, 165), and the latter converted into the ester through the agency of the silver salt; the ester crystallises in pale yellow leaflets melting at 76—77°. *Methyl* o-*azobenzoate,* prepared from the silver salt, crystallises in red needles melting at 101°; methyl *o*-azoxybenzoate, which has been previously prepared by Uspensky (*loc. cit.*), melts at 117° (corr.). K. J. P. O.

Benzeneazopyrroles and Benzeneazoindoles. Giuseppe Plancher and E. Soncini (*Gazzetta*, 1902, 32, ii, 447—466).—It has been shown that all so-called oxyazo-derivatives are, in the free state, phenylhydrazone compounds which possess, in greater or less degree, the power of changing into real oxyazo compounds; their alkali metal derivatives and their ethers also have an oxyazo-structure. The present researches have been made with a view to ascertaining whether the azopyrrole and azoindole derivatives also have a phenylhydrazone structure. To this end, their reactivity with phenylcarbimide has been examined, and it has been found that all the pyrrole or indole compounds having the azo-residue in the 2-position react, with different degrees of readiness, with the carbimide, whilst those in which the azo-residue occupies the 3-position do not. It cannot be concluded from this behaviour that the 3-azo-compounds are true azo-derivatives and that the 2-derivatives are really hydrazones, as it may be that, in the free state, all are azo-compounds differing in the facility with which they become transformed into hydrazones.

Phenylcarbimide does not react with pyrrole, 5-phenyl-2-methylpyrrole, or *s*- or *as*-dimethylpyrrole.

Pyrroleazobenzenephenylcarbamide, $C_4NH_3{:}N{\cdot}NPh{\cdot}CO{\cdot}NHPh$, prepared by the action of phenylcarbimide on benzeneazopyrrole, separates from light petroleum in orange-yellow, acicular crystals melting at 108—110°.

Benzeneazo-5-phenyl-2-methylpyrrole, $C_{17}H_{15}N_3$, separates from dilute alcohol in reddish-yellow crystals which soften at 105° and melt at 120° and are slightly soluble in benzene or light petroleum. It does not react with phenylcarbimide.

Benzeneazo-2 : 4-dimethylpyrrole, $C_{12}H_{13}N_3$, is deposited from dilute alcohol in shining, garnet-red crystals melting at 118—119° and soluble in benzene and, to a slight extent, in light petroleum; it has basic properties and forms a hydrochloride and a reddish-yellow picrate. It combines with phenylcarbimide, yielding *benzeneazo-2 : 4-dimethyl-*

pyrrolephenylcarbamide, $C_4NH_2Me_2{:}N{\cdot}NPh{\cdot}CO{\cdot}NHPh$, which separates from light petroleum in crystals melting at 72° and, when kept gradually decomposes into its components.

Benzeneazo-2 : 5-dimethylpyrrole does not react with phenylcarbimide.

Attempts to prepare azo-derivatives of indole and 3-methylindole (scatole) have not been successful.

Benzeneazo-2-phenylindole, $NH{<}\begin{smallmatrix}C_6H_4\\CPh\end{smallmatrix}{>}C{\cdot}N_2Ph$, separates from light petroleum or benzene in stable crystals melting at 166°. Like benzeneazo-2-methylindole, it does not react with phenylcarbimide.

The action of methyl iodide on pyrroleazobenzene yields methylpyrroleazobenzene as a red liquid which boils at 140° under 21 mm. pressure and forms an intensely red *hydrochloride*, a crystalline *platinichloride*, and a *picrate*, $C_{17}H_{14}O_7N_6$, separating from alcohol in crystals melting at 151°; on reduction, aniline is given off, showing that the methyl group does not replace a hydrogen of the phenylhydrazine residue, as if this were the case methylaniline would be obtained. T. H. P.

Syntheses with Phenylazoimide [Triazobenzene]. III. OTTO DIMROTH (*Ber.*, 1903, **36**, 909—913. Compare Abstr., 1902, i, 403; and this vol., i, 127).—Phenylazoimide (triazobenzene) reacts readily with an ethereal solution of phenylmagnesium bromide, yielding the *compound*, $MgBr{\cdot}NPh{\cdot}N{:}NPh$, which separates in the form of orange-red crystals when the ethereal solution is placed in ice. It is extremely unstable and reacts most readily with water, yielding diazoaminobenzene.

Triazobenzene also reacts with an ethereal solution of methylmagnesium iodide, yielding an additive product, which, on treatment with water and ammonium chloride solution, yields *diazobenzenemethylamide*, $NPh{:}N{\cdot}NHMe$ or $NHPh{\cdot}N{:}NMe$, in the form of large, colourless plates melting at 37—37·5° and readily soluble in most organic solvents. In contact with acids, or when warmed with water, it is hydrolysed to aniline, methyl alcohol (or ester), and free nitrogen. It methylates most acids as readily as does diazomethane. J. J. S.

The Iodine-binding Group in Proteid. ADOLF OSWALD (*Beitr. chem. Physiol. Path.*, 1903, **3**, 514—521).—From the study of iodine compounds of casein and gelatin and of the products of tryptic digestion, the conclusion is drawn that tyrosine is not the only iodine-binding group in the proteid molecule, but the nature of the other complex is not decided. W. D. H.

Products obtained by the Iodation of Proteids. III. C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1903, **37**, 350—354. Compare Abstr., 1902, i, 251, 732; and this vol., i, 135).—The aromatic compounds produced by the action of iodine on egg-albumin have been investigated. The conditions were the same as in the experiments previously described, and silver iodate was added in order to eliminate as far as possible the reducing action of the hydrogen iodide.

Among the products isolated were phenol and *p*-cresol, both decomposition products of tyrosine; also benzoic and hippuric acids, probably produced by the oxidising action of iodine on alanine, one of the primary decomposition products of tyrosine. J. J. S.

Ovomucoid. Leo Langstein (*Beitr. chem. Physiol. Path.*, 1903, 3, 510—513).—The conclusion is reached that ovomucoid is preformed in white of egg; the results of elementary analysis come out very close to those of previous observers. Its amount is fairly constant. Its place in a classification of proteids is discussed.

W. D. H.

Optical Activity of Hæmoglobin and of Globin. Arthur Gamgee and A. Croft Hill (*Proc. Roy. Soc.*, 1903, 71, 376—385; *Ber.*, 1903, 36, 913—914).—Solutions of hæmoglobin and its derivatives have been examined in a large Lippich half-shadow polarimeter specially constructed for investigations with polarised light of any wave length. A Landolt's filter for red rays was employed, and by this means a monochromatic light of mean wave length $\lambda = 665{\cdot}3\ \mu\mu$ was obtained.

Hæmoglobin, oxyhæmoglobin, and carbon monoxide hæmoglobin have $[\alpha]_c + 10{\cdot}4$. These are the first examples of dextrorotatory proteid substances. Globin has $[\alpha]_c - 54{\cdot}2$. J. J. S.

Optical Activity of Nucleoproteids from the Pancreas, Thymus, and Secondary Nerves. Arthur Gamgee and Walter Jones (*Proc. Roy. Soc.*, 1903, 71, 385—397; *Ber.*, 1903, 36, 914. Compare preceding abstract).—The nucleoproteids are all dextrorotatory. Nucleohiston from thymus has $[\alpha]_D + 37{\cdot}5°$, and Hammarsten's nucleoproteid from the pancreas has $[\alpha]_D + 97{\cdot}9°$. On transformation into a nuclein, the optical activity of the nucleoproteid is lessened.

J. J. S.

Cytosine. Albrecht Kossel and H. Steudel (*Zeit. physiol. Chem.*, 1903, 37, 377—380).—Cytosine from thymusnucleic acid (Kossel and Neumann, Abstr., 1894, i, 156; 1896, i, 658) has been further investigated. Analyses of the platinichloride and of the picrate indicate that the formula for the free base is $C_4H_5ON_3$ and not $C_{21}H_{30}O_4N_{16}$ as previously suggested. The picrate can only be obtained pure by using a specimen of the base purified by the aid of its platinichloride. It crystallises in pale yellow, glistening needles, turns brown at 255°, and melts and decomposes at 270° (uncorr.). The base is undoubtedly identical with the cytosine recently obtained from the testicles of the sturgeon (this vol., i, 303). The reactions of the base with chlorine water and with nitrous acid, indicate that it is an iminohydroxypyrimidine. J. J. S.

A Soluble Modification of Plastein. W. W. Sawjaloff (*Chem. Centr.*, 1903, i, 529; from *Centr. Physiol.*, 16, 625—627).—The substance formed by the action of rennet on albumoses exists also in

a soluble form. After albumoses from fibrin are allowed to remain at room temperature with gastric juice, the fluid contains coagulable proteid and the coagulum shows all the properties of plastein. W. D. H.

Uroferric Acid. O. Thiele (*Zeit. physiol. Chem.*, 1903, 37, 251—301).—*Uroferric acid*, $C_{35}H_{56}O_{19}N_8S$, is obtained from urine by a lengthy process described in the original paper. The *zinc* salt, $C_{35}H_{50}O_{19}N_8SZn_3$, and *barium* salt, $C_{35}H_{50}O_{19}N_8SBa_3$, have been prepared; both are soluble in water, but are precipitated by absolute alcohol. When quite free from ether, the acid is only slightly hygroscopic, it dissolves readily in water, saturated ammonium sulphate solution, or in dry methyl alcohol, yielding pale yellow, or, when concentrated, dark brown, solutions. It is only sparingly soluble in absolute alcohol and is insoluble in most other organic solvents. It has a strongly acid reaction, bitter taste, and gives negative results with Millon's, Adamkiewicz', and Molisch's reagents, also in the xanthoprotein reaction, and with mercuric chloride, metaphosphoric acid, and picric acid solutions. Prolonged boiling with alkaline lead acetate does not remove any of the sulphur. It yields precipitates with phosphotungstic acid and with mercury sulphate or nitrate. The acid is optically active in solution and has $[\alpha]$ $-32\cdot5°$ at 18°. When decomposed at 145° with hydrochloric acid of sp. gr. 1·12, it yields carbon dioxide and other products which have not been identified. Arginine and histidine were not present. Decomposition with hydrochloric acid and stannous chloride under the ordinary pressure gives rise to hydrogen sulphide, sulphuric acid, aspartic acid, ammonia, and small amounts of organic amines, but none of the known hexone bases. J. J. S.

General Characters of the Soluble Ferments which effect the Hydrolysis of the Polysaccharides. Émile Bourquelot (*Compt. rend.*, 1903, 136, 762—764. Compare Abstr., 1902, i, 744). —Attempts are made to define the relation which exists between the soluble ferments and the substances (sugars) on which they exert their action. Each of the hexobioses formed by the condensation of two mols. of dextrose, namely, maltose, trehalose, gentiobiose, and touranose, requires a different ferment to convert it into dextrose; the ferment can only attack one type of linking. In the same way, the hexobioses formed from dextrose and another hexose are each hydrolysed by its special ferment. In the hexotrioses, such as gentianose, two ferments are frequently required to completely hydrolyse the polysaccharide; thus, in the case quoted, invertase produces gentiobiose and lævulose, but the gentiobiose can only be hydrolysed by the subsequent action of gentiobiase; further, the invertase must act first; gentiobiase has no action on the triose. In the case of the hexotetroses, three ferments are required to act successively and in a given sequence, but one ferment may be required twice at different periods of the hydrolysis.

K. J. P. O.

Organic Chemistry.

New Method of Preparation of Nitrolic Acids. Giacomo Ponzio (*Atti R. Accad. Sci. Torino*, 1903, **38**, 201—205).—Nitrolic acids may be readily prepared by the action of an ethereal solution of nitrogen peroxide (1 mol.) on the *a-iso*nitroso-acids (1 mol.) of the fatty series. The energy of the reaction may be controlled by cooling the flask in which the reaction is proceeding. The resulting solution is afterwards washed with a little water and the nitrolic acid is then extracted as potassium salt by treatment with 10 per cent. potassium hydroxide solution.

Methylnitrolic acid, prepared in this way from *iso*nitrosoacetic acid, crystallises from a mixture of ether and light petroleum in long, flattened needles melting and decomposing at 68°, and not at 64°, as was stated by Tscherniac (Abstr., 1875, 560).

The melting point of the ethylnitrolic acid obtained confirms that given by Nef (*Annalen*, 1894, **280**, 283; Abstr., 1895, i, 3).

The *benzoyl* derivative of propylnitrolic acid crystallises from alcohol in faintly yellow laminæ which melt at 85°, and are soluble in light petroleum or chloroform. T. H. P.

Catalytic Decomposition of Ethyl Alcohol. Wladimir N. Ipatieff (*J. pr. Chem.*, 1903, [ii], **67**, 420—421. Compare Abstr., 1902, i, 4, 335, and Ehrenfeld, Abstr., 1903, i, 306).—The author's previous papers (*loc. cit.*) on the influence of catalytic agents and of various temperatures on the decomposition of alcohols have been overlooked by Ehrenfeld.

When distilled over aluminium powder at 580—680°, ethyl alcohol yields divinyl in addition to the products of the aldehyde and ethylene decompositions.

With bromine, divinyl forms the tetrabromide, which melts at 115—116° and, when treated with alcohol and zinc dust, yields a *hydrocarbon*, C_4H_6. When passed through a solution of hydrogen bromide in glacial acetic acid, this forms an unsaturated *bromide*, C_4H_7Br, which melts at 102—107°, forms an additive product with bromine, and decolorises potassium permanganate. When distilled over aluminium at 620—700°, ethylene yields hydrogen, carbon, and methane. Under the same conditions, water is not decomposed.

G. Y.

Catalytic Decomposition of Alcohols by Finely-divided Metals. Saturated Primary Alcohols. Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1903, **136**, 921—924. Compare this vol., i, 393).—Reduced copper decomposes primary saturated alcohols according to the equation $C_nH_{2n+1}\cdot CH_2\cdot OH = H_2 + C_nH_{2n+1}\cdot COH$, giving hydrogen and an aldehyde. This may conveniently be used as a method for preparing aldehydes. The decomposition of the alcohols

takes place at about 200—240°, but at higher temperatures the aldehyde formed is more or less destroyed with the production of carbon monoxide and a hydrocarbon; at about 400°, the decomposition of the aldehyde is practically complete.

With reduced nickel, the action is more violent and takes place at a lower temperature, but it is impossible to avoid the partial decomposition of the aldehyde formed. The action is further complicated by the fact that nickel decomposes the carbon monoxide formed from the aldehyde. Reduced cobalt acts similarly to nickel.

Platinum sponge also effects the decomposition of the alcohol, but at a temperature superior to that required with copper, and consequently there is a greater destruction of the aldehyde than when copper is employed. J. McC.

Catalytic Decomposition of Alcohols by Finely-divided Metals. Allyl and Benzyl Alcohols. Secondary and Tertiary Alcohols. Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1903, **136**, 983—986. Compare this vol., i, 393, and preceding abstract).—Reduced copper acts on allyl alcohol at 180° giving hydrogen and an unsaturated aldehyde, but the aldehyde is then reduced by the hydrogen and the products of the decomposition are propaldehyde and a small quantity of hydrogen and acraldehyde ($CH_2\dot{.}CH\cdot CH_2OH = H_2 + CH_2\dot{.}CH\cdot COH$; $CH_2\dot{.}CH\cdot COH + H_2 = CH_3\cdot CH_2\cdot COH$). At 300°, reduced copper decomposes benzyl alcohol, giving hydrogen and benzaldehyde. At 380°, the reaction is more complex, and amongst the products are found hydrogen, carbon monoxide, carbon dioxide, benzene, and toluene, produced according to the two equations: $CH_2Ph\cdot OH = C_6H_6 + CO + H_2$ and $2CH_2Ph\cdot OH = C_6H_5Me + C_6H_6 + CO_2 + H_2$. This decomposition may also be brought about by reduced nickel, but there is a greater decomposition of the benzaldehyde formed.

Secondary alcohols are similarly decomposed by reduced metals, and the actions are simpler because the ketones formed are more stable than the aldehydes formed from the primary alcohols. All the secondary alcohols examined are decomposed by reduced copper, giving pure hydrogen and a 75 per cent. yield of the ketone. In this way, *iso*propyl alcohol gives acetone slowly at 150° and quite smoothly at 250—430°. *iso*Butyl alcohol is decomposed at 160°, and up to 300° there is no decomposition of the ketone formed. Methylhexylcarbinol is decomposed at 250—300°; at 400°, there is a slight decomposition into carbon monoxide, methane, and hexane. Reduced nickel also effects this decomposition, but at the same time the ketone is always more or less decomposed. At 210°, *iso*propyl alcohol gives water, methane, and ethane ($CHMe_2\cdot OH + H_2 = H_2O + CH_4 + C_2H_6$), as well as hydrogen and acetone. At 260°, the reaction is more complex and carbon monoxide and carbon dioxide are formed; no aldehyde, however, is produced. At 200°, *iso*butyl alcohol gives hydrogen and methyl ethyl ketone, but at the same time about half of the alcohol is decomposed into water and a paraffin hydrocarbon. Methylhexylcarbinol is similarly decomposed at 250°.

In its action, reduced cobalt stands about midway between copper and nickel in bringing about the decomposition of secondary alcohols.

Platinum sponge decomposes *iso*propyl alcohol into acetone and hydrogen at 300° without any further decomposition, and even at 400° only a comparatively small amount of carbon monoxide is formed.

Tertiary alcohols are also decomposed by reduced metals. At 280—400°, reduced copper decomposes trimethylcarbinol into *iso*butylene and water, whilst at 300° *tert.*-amyl alcohol gives water and β-methylbutylene. Analogous results are obtained with reduced nickel at temperatures up to 200°, but at higher temperatures the olefinic hydrocarbon is decomposed into carbon and a paraffin hydrocarbon. J. McC.

Physical Properties of Trimethylcarbinol. ROBERT DE FORCRAND (*Compt. rend.*, 1903, 136, 1034—1037. Compare Abstr., 1892, 1066).—Trimethylcarbinol, purified by distillation with metallic sodium, melts at 25·45°, boils at 82·8° (corr.) under 761·4 mm. pressure, and when slowly sublimed forms large, flattened, orthorhombic prisms. The specific heat of the salt between the temperatures −21° and 14° is 0·580, and of the liquid between the temperatures 25·45° and 44·8°, 0·722. The molecular heats of liquefaction and vaporisation are 1·552 and 9·426 respectively. T. A. H.

Action of Carbonyl Chloride on Mixed Organo-magnesium Compounds. VICTOR GRIGNARD (*Compt. rend.*, 1903, 136, 815—817). —When the commercial 20 per cent. solution of carbonyl chloride (1 mol.) in toluene is treated with an organo-magnesium compound (3 mols.), a tertiary alcohol is formed, and, in the case of the higher alkyl compounds, also secondary alcohols: $COCl_2 + 3RMgX = CR_3{\cdot}O{\cdot}MgX + 2MgXCl$. Thus, from magnesium methyl iodide and ethyl bromide, trimethylcarbinol and triethylcarbinol are obtained in yields equal to 50 per cent. of the theoretical; from magnesium propyl bromide, a mixture of dipropylcarbinol and *tripropylcarbinol* is formed; the latter is a mobile liquid of strong odour, boiling at 190—192°. Magnesium *iso*amyl bromide gives a mixture of di*iso*amylcarbinol and *triisoamylcarbinol*; the latter is a very viscous liquid of sweet odour boiling at 140° under 10 mm. pressure.

When carbonyl chloride (1 mol.) and the organo-magnesium compound (2 mols.) are used, besides the primary and tertiary carbinols, the products of dehydration of these substances are formed. Thus, from magnesium *iso*amyl bromide, the hydrocarbon,

$$C(C_5H_{11})_2{:}CH{\cdot}CH_2{\cdot}CHMe_2,$$

is obtained as a mobile liquid boiling at 114—115° under 10 mm. pressure.

Under no circumstances does the ketone, which might be expected, appear to be formed. K. J. P. O.

Action of Alkalis on Glycerol: Estimation of Glycerol. A. BUISINE (*Compt. rend.*, 1903, 136, 1082—1083).—When glycerol is heated with excess of potassium hydroxide or potash-lime at 220—250°, potassium formate and acetate are formed; at 250—280°, potassium

acetate and oxalate are the principal products; whilst at 280—320° acetate and carbonate of potassium are produced. In each reaction, a definite volume of hydrogen is evolved, and it is suggested that glycerol might be estimated by heating with a large excess of potassium hydroxide and potash lime at 320° and measuring the volume of hydrogen. T. A. H.

Action of Phosphorous Acid on Erythritol. P. CARRÉ (*Compt. rend.*, 1903, **136**, 1067—1069. Compare this vol., i, 307).—When molecular quantities of phosphorous acid and erythritol are heated at 130°, there is formed, after one hour, the monoerythritol ester, and after some hours the *compound* $C_2H_2(OH)_2[CH_2 \cdot O \cdot P(OH)_2]_2$. These substances were isolated as their calcium salts. When the reaction is continued for 150 hours, the principal product is *erythran phosphite*, $P(OH)C_4H_6O_3$; this crystallises in colourless needles, melts at 117°, sublimes at 130—140°, and is decomposed by water forming the *acid ester*, $P(OH)_2 \cdot O \cdot C_4H_7O_2$. The *calcium* salt of this crystallises in needles containing H_2O, and becomes anhydrous at 100°.

T. A. H.

The Simplest Chloro-ethers. EDGAR WEDEKIND (*Ber.*, 1903, **36**, 1383—1386).—Chloromethyl methyl ether, $CH_2Cl \cdot OMe$, is best prepared by triturating trioxymethylene with methyl alcohol saturated with hydrogen chloride; it boils rather indefinitely at about 60°, and is rapidly decomposed by water, giving a solution of formaldehyde, methyl alcohol, and hydrogen chloride. Trioxymethylene is obtained, contrary to former statements, only when the decomposition is slowly effected by an insufficient quantity of water. When the chloro-ethers interact with salts of organic acids, esters of the type $CO_2R \cdot CH_2 \cdot OR'$ are formed, but the facility of interaction varies greatly; thus, from potassium acetate and chlorodimethyl ether and chloromethyl ethyl ether, the esters $CH_3 \cdot CO_2 \cdot CH_2 \cdot OMe$ and $CH_3 \cdot CO_2 \cdot CH_2OEt$ are easily obtained, but the corresponding esters of formic acid are not producible from potassium or calcium formate, but only from lead formate.

W. A. D.

Action of Mineral Acids on Acetic Acid. AMÉ PICTET (*Arch. Sci. phys. nat.*, 1903, [iv], **15**, 465—467. Compare this vol., i, 309).—By the action of chromic anhydride on glacial acetic acid, *acetic chromic anhydride*, $OH \cdot CrO_2 \cdot OAc$, is produced, and forms, after drying at 110°, a brownish-red powder, which decomposes on heating, yielding chromic oxide. All the mixed anhydrides are decomposed by water into the corresponding acids, and, with the exception of triacetic boric anhydride (*loc. cit.*), yield ethyl acetate on treatment with alcohol, whilst ammonia gives acetamide and the ammonium salt of the mineral acid. G. D. L.

Plumbic Acid Derivatives. ALBERT COLSON (*Compt. rend.*, 1903, **136**, 891—892. Compare this vol., i, 396).—The author acknowledges the work of Hutchinson and Pollard (Trans., 1893, **69**, 212). Lead

tetra-acetate can be conveniently prepared by passing a current of chlorine through an acetic acid solution of lead acetate. The lead tetra-acetate is separated from the lead chloride formed by means of hot acetic acid. J. McC.

Natural and Synthesised Palmityldistearins. HANS KREIS and AUGUST HAFNER (*Ber.*, 1903, **36**, 1123—1128).—The authors have prepared Guth's $\alpha\beta$-distearin (this vol., i, 225) by heating together glycerol and stearic acid at 200° for 8 hours. From this, α-palmityldistearin (Guth, *loc. cit.*) was prepared by heating with palmitic acid at 200° for 16 hours.

The crystalline fat prepared by Hansen (Abstr., 1902, i, 339) and by the authors (Abstr., 1902, i, 529) by fractional crystallisation of lard and beef fat is shown to be α-palmityldistearin, whilst that from mutton fat is an isomeride (β-palmityldistearin ?) which has not yet been synthesised. The foregoing glycerides possess double melting points under the conditions already recorded (Abstr., 1902, i, 529); they are not changed by recrystallisation from boiling amyl alcohol (Hansen, *loc. cit.*). T. A. H.

Camphocarboxylic Acid. VI. JULIUS W. BRÜHL (*Ber.*, 1903, **36**, 1305—1313. Compare this vol., i, 314).—Camphocarboxylic acid can be prepared by the action of carbon dioxide on the product of interaction of camphor in benzene solution with sodamide; in this method of preparation, no reduction to borneol takes place, and the only bye-product is a little unchanged camphor. α-Bromocamphor also yields camphocarboxylic acid by this method.

The acid salt, $C_{22}H_{31}O_6Na$, which is readily soluble in benzene, gives only a pale brown tint when shaken with aqueous ferric chloride in the cold, but as the solution is warmed, a deep violet colour appears, which vanishes again on cooling; this change can be observed repeatedly with the same sample of material, and is regarded as indicating that the acid salt in benzene solution is entirely ketonic at the ordinary temperature, and only becomes enolic when warmed.

Amyl camphocarboxylate is much less soluble both in water and alkalis than the methyl ester, and the solubility of the latter in alkalis is greatly decreased by diluting or cooling, or by the addition of salt.

The sodium salt of the methyl ester does not interact with copper bromide or with mercuric chloride in benzene solution, but gives a precipitate, probably $C_8H_{14}<\begin{matrix}C(CO_2Me)HgCl \\ | \\ CO\end{matrix}$, with aqueous mercuric chloride, and also interacts with copper chloride in methyl alcohol. T. M. L.

Organic Acids. WILLIAM ŒCHSNER DE CONINCK and RAYNAUD (*Compt. rend.*, 1903, **136**, 817—818. Compare this vol., i, 231).—When the following acids are heated with sulphuric acid, they are decomposed, carbon dioxide being produced; pyrotartaric, fumaric, mucic, hippuric, aspartic, benzoic, aminobenzoic, nitrobenzoic, hydroxy-

benzoic, *o*- and *p*-toluic, phenylacetic, phenylglycollic, phthalic, anisic, quinic, cinnamic, chrysophanic, protocatechuic, tannic, and gallic acids. Camphoric acid, under the same conditions, yields a mixture of carbon mon- and di-oxide. When heated with glycerol, the following acids are not decomposed: fumaric, phthalic, benzoic, cinnamic, *m*-hydroxybenzoic, and chrysophanic acids; the following are decomposed, giving only a trace of carbon dioxide: *m*-aminobenzoic, camphoric, *o*-toluic, phenylacetic, phenylglycollic, and pyrotartaric acids; the following are decomposed, giving moderate quantities of carbon dioxide: gallic, tannic, *o*- and *p*-aminobenzoic, nitrobenzoic, *p*-toluic, protocatechuic, *p*-hydroxybenzoic, and salicylic acids.

The stability of the isomeric aromatic acids is very different at the boiling point of their solutions in glycerol; even after prolonged heating, *m*-aminobenzoic acid is not decomposed, whereas the ortho-acid is easily decomposed, whilst the para-acid occupies an intermediate position. K. J. P. O.

Organic Acids. William Œchsner de Coninck and Raynaud (*Compt. rend.*, 1903, **136**, 1069—1070. Compare this vol., i, 231).—The stabilities of acetic, propionic, butyric, and valeric acids towards a large excess of hot sulphuric acid diminish as the series is ascended, whilst the stabilities of *iso*butyric and *iso*valeric acids, under these conditions, are much less than those of the normal acids. Benzoic acid is sulphonated by this reagent, but also partially decomposed with the liberation of carbon dioxide and the formation of benzenesulphonic acid.

Phthalic acid is highly resistant towards hot sulphuric acid; phthalic anhydride is first formed, and later benzoic acid, which then decomposes as described, and eventually the phthalic acid undergoes sulphonation. T. A. H.

Velocity of Hydrolysis of and Affinity Constants of Ethyl Malonate. Heinrich Goldschmidt and Victor Scholz (*Ber.*, 1903, **36**, 1333—1341. Compare Abstr., 1900, i, 132, 373).—The hydrolysis of ethyl potassium malonate by aqueous sodium hydroxide at 25° has been examined. The results prove that the reaction is one of the second order, and the mean value for K is 1·27, using $0·05N$ solutions of the alkali and ester.

When ethyl malonate is mixed with one equivalent of sodium hydroxide solution and left for an hour, it is converted practically quantitatively into the acid ester, as on the addition of a further equivalent of alkali and a study of the velocity of hydrolysis, the same value for K, namely, 1·27 is obtained. The velocity of hydrolysis of the normal ester to the acid ester has also been studied using solutions of 0·005 normality. At the end of specified times, excess of $0·1N$ hydrochloric acid was added and the excess titrated with standard ammonia solution, using *p*-nitrophenol or Kubel and Tiemann's litmus solution as indicator. The mean value for K, using the equation for a bimolecular reaction, is 112·4. The values for K vary somewhat and show a tendency to decrease with the time. This has been shown to be due to the difficulty in titration due to the hydrolysis of the

salt formed. The value for K is not affected by altering the concentration or by the addition of alcohol and sodium chloride.

From the fact that the constant is independent of the concentration, the conclusion is drawn that the ester in aqueous solution has practically no acid properties and is not ionised. The ester is thus a much less acidic compound than ethyl acetoacetate. The high values obtained by Vorländer (this vol., i, 230) are due to the fact that it is very difficult to obtain correct conductivity values for extremely feeble electrolytes (Walker, Abstr., 1900, ii, 268). J. J. S.

Chromomalonates. JAMES L. HOWE (*J. Amer. Chem. Soc.*, 1903, **25**, 444—446).—A monobasic chromomalonic acid, $HCr(C_3H_2O_4)_2 \cdot 2H_2O$, was prepared by the action of malonic acid on chromium hydroxide; it forms pink crystals which are not pleochroic. Its *pyridine* and *potassium* salts are monoclinic and exhibit pleochroism. Tribasic chromomalonic acid, $H_3Cr(C_3H_2O_4)_3,3H_2O$, formed from chromium hydroxide and excess of malonic acid, is a pale pink powder.

A. McK.

Reduction of Glutaric Anhydride to δ-Valerolactone. FRITZ FICHTER and ALFRED BEISSWENGER (*Ber.*, 1903, **36**, 1200—1205. Compare Abstr., 1896, i, 463).—A mixture of glutaric and δ-hydroxyvaleric acids is obtained when glutaric anhydride is reduced with aluminium amalgam in ethereal solution. These may be separated by the aid of their barium salts, as barium δ-hydroxyvalerate is readily soluble in alcohol. To obtain the lactone, the syrupy barium salt is dissolved in water and acidified, the solution boiled, then neutralised with sodium carbonate, and extracted with ether. About 1/4th of the lactone is thus obtained in the form of a colourless oil distilling at 113—114° under 13—14 mm. pressure.

The lactone readily polymerises to a crystalline compound melting at 47—48°, and readily soluble in most organic solvents with the exception of light petroleum.

When δ-hydroxy-α-methylglutaric acid is distilled, it yields an acid identical with von Pechmann and Röhm's α-methyleneglutaric acid (Abstr., 1901, i, 253), together with a small amount of the lactone of the same acid. The lactone was erroneously described by Weidel (Abstr., 1890, 734) as δ-valerolactone, and the acid by Smoluchowski (Abstr., 1894, i, 343) as α-methylglutaconic acid. The dissociation constant k for the acid is 0·0067.

A 5 per cent. yield of *β-ethyl-γ-butyrolactone*, $\begin{matrix} CHEt\cdot CH_2 \\ | \\ CH_2 \text{——} CO \end{matrix}\!\!>\!O$, is obtained when ethylsuccinic anhydride is reduced; it is a colourless oil distilling at 218—219°. The *barium*, *calcium* ($2H_2O$), and *silver* salts of the corresponding hydroxy-acid have been prepared.

α-Methylglutaric anhydride, when reduced, yields a small amount of a *methyl-δ-valerolactone* distilling at 104—108° under 13—14 mm. pressure. J. J. S.

1-Methyl-2 : 3 : 3-trimethylenetricarboxylic Acid. ERNST PREISWECK (*Ber.*, 1903, **36**, 1085—1087).—Ethyl α-bromocrotonate

may be conveniently prepared by the action of sodium ethoxide on ethyl $\alpha\beta$-dibromobutyrate and boils at 95—97° under 15 mm. pressure, but appears to be contaminated with a little ethyl tetrolate. On condensation with ethyl sodiomalonate, ethyl α-bromo-(or chloro-)-crotonate gives ethyl 1-methyltrimethylene-2 : 3 : 3-tricarboxylate, boiling at 163—164° under 15 mm. pressure, and not an ethylidene-ethanetricarboxylate as supposed by Hjelt (Abstr., 1885, 243).

The monoethyl ester of the tricarboxylic acid forms a sparingly soluble potassium salt and an amorphous silver salt; it crystallises with $2H_2O$ and melts at 70—71°, or when anhydrous at 150°.

1-Methyltrimethylene-2 : 3 : 3-tricarboxylic acid, prepared from the barium salt, forms a crystalline powder, decomposes at 215°, forming the anhydride of *1-methyltrimethylene-2 : 3-dicarboxylic acid* as an oil, from which the *cis*-acid, melting at 108°, is obtained on evaporating the aqueous solution. On heating the tricarboxylic acid with water at 210°, methylitaconic and methylparaconic acids are formed.

G. D. L.

Action of Formaldehyde on *iso*Valeraldehyde and on Œnanthaldehyde. C. M. van Marle and Bernhard Tollens (*Ber.*, 1903, **36**, 1341—1347. Compare Abstr., 1892, 128; 1893, i, 617; 1894, i, 353, 438; 1896, i, 115).—*Dimethylpentaglycerol* (*γ-methyl ββ-dimethylol-α-butanol*), $CHMe_2\cdot C(CH_2\cdot OH)_3$, is obtained when *iso*-valeraldehyde is shaken with 40 per cent. formaldehyde solution and water at 30—35° for 24—36 hours. The fraction distilling at 180—200° under reduced pressure yields crystals of the compound melting at 83—83·5°.

The *triacetyl* derivative distils at 196—199° under reduced pressure and melts at 33—34°. The *tribenzoyl* derivative melts at 55°.

No definite crystalline compound has been obtained from œnanthaldehyde and formaldehyde.

J. J. S.

Action of Alcoholic Potash on Methylethylacraldehyde. Arthur von Lenz (*Monatsh.*, 1903, **24**, 155—166).—When acted on by excess of potassium hydroxide in alcoholic solution, methylethylacraldehyde undergoes condensation, three products being formed, methylacrylic acid, a glycol, and an ester. The *glycol*, probably $CHEt\colon CMe\cdot[CH\cdot OH]_2\cdot CMe\colon CHEt$, boils at 165—170° under 11 mm. pressure and crystallises in long, colourless needles melting at 89·5° and easily soluble in most organic solvents. Analysis and a determination of molecular weight by the freezing point method shows it to have the composition $C_{12}H_{22}O_2$; it unites with four atoms of bromine, and forms a *diacetate*, $C_{12}H_{20}O_2(COCH_3)_2$, boiling at 166—170° under 13 mm. pressure. When heated for four hours at 120° with 12 per cent. sulphuric acid, it loses a molecule of water and forms a compound $C_{12}H_{20}O$, a yellow liquid with a camphor-like odour, boiling at 115—117° under 30 mm. pressure.

The *ester*, $C_{18}H_{30}O_3$, is the simple methylethylacrylate of the glycol, and boils at 198—205° under 11 mm. pressure. It forms a *monoacetate* boiling at 225—232° under 11 mm. pressure, and is the

sole condensation product obtained when only a small amount of potassium hydroxide is employed; in presence of excess of alkali, however, the glycol and acid are produced. E. F. A.

β-Nitroso*iso*propylacetone [Methyl β-Nitroso*iso*butyl Ketone]. CARL D. HARRIES (*Ber.*, 1903, 36, 1069—1070. Compare Harries and Jablonski, Abstr., 1898, i, 400, and Bamberger and Seligman, this vol., i, 322).—The bimolecular modification of this compound melts at 75—76°, passing into the blue liquid unimolecular form, which distils without change at 59—60° under 10—11 mm. pressure, and with partial decomposition at 157—158° (corr.) under 765 mm. pressure. The liquid modification is decomposed by hot sodium hydroxide, but the solid form is not affected until it is heated above its melting point with the hydroxide, when it is suddenly decomposed with evolution of gas, having previously been transformed into the liquid modification. On the other hand, when the liquid form is poured into aqueous sodium hydroxide at the ordinary temperature, it is largely transformed into the solid modification.

G. D. L.

Resolution of Racemic Aldehydes and Ketones. CARL NEUBERG (*Ber.*, 1903, 36, 1192—1194).—The use of an optically active hydrazine is suggested as a means of resolving racemic forms of aldehydes, ketones, and acids. *i*-Arabinose combines, for instance, with *l*-menthylhydrazine in alcoholic solution to form a sparingly soluble d-*arabinose* l-*menthylhydrazine*, which separates in prisms; on concentrating the mother liquors, a syrup, consisting principally of the hydrazone of *l*-arabinose, is obtained. The active aldehyde or ketone can be isolated from its hydrazone by the action of formaldehyde.

W. A. D.

Soluble Cellulose. LÉO VIGNON (*Compt. rend.*, 1903, 136, 969—970. Compare Abstr., 1898, i, 8).—Oxycellulose, when treated with potassium hydroxide solution is partially dissolved, giving a golden-yellow solution, but 60 per cent. reverts to ordinary cellulose. The dissolved part can be precipitated by acids. The precipitate, when dried at the ordinary temperature, forms a white, amorphous powder and contains 3·5 per cent. of water, which it loses at 110°. It has the same composition as cellulose, but differs from it in heat of combustion and in the ease with which it forms furfuraldehyde. It is soluble to the extent of 0·396 gram per litre in hot water, and is insoluble in ether, alcohol, benzene, chloroform, acetone, or carbon disulphide. It is dissolved by alkalis giving yellow solutions which become brown on standing, and is reprecipitated by acids or solutions of the chlorides of potassium, sodium, barium, or calcium. Hydrochloric acid dissolves it partially, nitric acid completely, and it is carbonised by sulphuric acid. It reduces Fehling's solution and gives a pink coloration with Schiff's reagent. J. McC.

Constitution of Nitrocelluloses. LÉO VIGNON (*Compt. rend.*, 1903, **136**, 818—820. Compare Abstr., 1900, i, 589, 628, 629; 1901, i, 662; 1902, i, 9).—A cellulose nitrate containing 13·89 per cent. of nitrogen is readily obtained by treating dry cotton with a mixture of sulphuric acid (63·35 grams), nitric acid (25·31 grams), and water (11·34 grams); when a mixture of sulphuric acid (3 parts) and nitric acid (1 part) is used, a cellulose nitrate containing 13·4 per cent. nitrogen is formed. By boiling with a saturated acid solution of ferrous chloride, these two cellulose nitrates are converted into oxycelluloses free from nitrogen. K. J. P. O.

Nitrated Cellulose. LÉO VIGNON (*Compt. rend.*, 1903, **136**, 898—899. Compare Abstr., 1900, i, 242).—The oxycellulose obtained by the action of potassium chlorate and hydrochloric acid on cellulose, is a definite chemical compound, the composition of which is to be represented by $C_{24}H_{40}O_{21}(=3C_6H_{10}O_5+C_6H_{10}O_6)$. In nitrating cellulose to the greatest possible extent, a certain amount of oxycellulose is produced, and the nitration product is to be represented by $C_{24}H_{28}O_{45}N_{12}(=3C_6H_7(NO_2)_3O_5+C_6H_7(NO_2)_3O_6)$. J. McC.

Periodides. DANIEL STRÖMHOLM (*J. pr. Chem.*, 1903, [ii], **67**, 345—356. Compare this vol., i, 138; Geuther, Abstr., 1887, 910).—Periodides belong to the types RI,I_2, RI,I_4, RI,I_6, and RI,I_8. No periodide belonging to a type higher than the last is known. The existence of periodides of types such as RI,I or RI,I_5 is very doubtful. The tri-iodides are brown or brownish-violet, the pentaiodides are usually green, the heptaiodides are, with the exception of tetraethylammonium heptaiodide, of a dark colour, the enneaiodides are dark green.

Tetramethylammonium enneaiodide melts at 108° (Geuther, 110°) and is converted into the pentaiodide when shaken with ether. Treatment with concentrated ethereal iodine solution converts the pentaiodide, and more slowly the tri-iodide, into the enneaiodide.

Tetraethylammonium heptaiodide is dark violet, forms no additive product with iodine, and when shaken with ether yields the tri-iodide.

Trimethylethylammonium enneaiodide melts at 67° (Geuther, 38°) and by treatment with ether is converted into the pentaiodide, which melts at 68° (Müller, *Annalen*, 1857, **108**, 1), and unites with iodine in ethereal solution with formation of the enneaiodide.

Methyltriethylammonium heptaiodide is converted into the pentaiodide by ether. The formation of an enneaiodide is doubtful.

The action of an ethereal solution of iodine on phenyltrimethylammonium pentaiodide leads to the formation of the *enneaiodide*, which melts at 69°, and by treatment with ether is converted successively into the hepta-, penta-, and tri-iodides.

Phenyldimethylethylammonium enneaiodide melts at 29°, and on treatment with dilute ethereal iodine solution yields the heptaiodide, which is converted by ether into the pentaiodide.

Hexamethyltrimethylenediammonium iodide forms an *enneaiodide*, $C_9H_{24}N_2I_2,I_{16}$, which melts at 100°, a *pentaiodide*, $C_9H_{24}N_2I_2,I_8$,

which melts at about 150°, and a *tri-iodide*, $C_9H_{24}N_2I_2,I_4$, which melts at 205°.

Tetramethylpiperazinium iodide, $C_8H_{20}N_2I_2$, forms a *pentaiodide*, $C_8H_{10}N_2I_2,I_8$, which melts and decomposes at 120°, and a *tri-iodide*, $C_8H_{10}N_2I_2,I_4$, which melts and boils at 215°. A hepta- or ennea-iodide was not formed. G. Y.

New Bases Derived from Pentoses. E. Roux (*Compt. rend.*, 1903, 136, 1079—1081. Compare Maquenne and Roux, Abstr., 1901, i, 372; and 1902, i, 266, and 695).—*Arabinamine*,

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}NH_2,$$

prepared by reducing arabinoseoxime with sodium amalgam, is a white, semicrystalline substance, which melts at 98—99°, possesses a bitter but slightly sweet taste, has $[\alpha]_D$ $-4{\cdot}58°$, and shows no mutarotation. It absorbs carbon dioxide from the atmosphere, displaces ammonia, and is reduced by hydriodic acid to amylamine. The *oxalate*,

$$2C_5H_{13}O_4N,H_2C_2O_4,$$

forms prismatic needles, melts at 189—190°, and has $[\alpha]_D$ $-13{\cdot}5°$ without mutarotation. The *oxamide*, $C_{12}H_{24}O_{10}N_2$, prepared by heating the oxalate, forms rectangular leaflets and melts at 217—218°. The *platinichloride* forms fine, yellow needles, and the *hydrochloride*, *hydriodide*, and *picrate* are all crystalline.

Arabinaminecarbamide, $C_5H_{11}O_4{\cdot}NH{\cdot}CO{\cdot}NH_2$, prepared from arabinamine sulphate and potassium cyanide, forms colourless needles and melts at 152—153°. The *phenylcarbamide*, $C_5H_{11}O_4{\cdot}NH{\cdot}CO{\cdot}NHPh$, produced by interaction of phenylcarbimide with the amine in pyridine solution, crystallises in groups of spear-shaped lamellæ and melts at 179°; with excess of phenylcarbimide, a *tetraphenylcarbamic phenylcarbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_5H_7O_4(CO{\cdot}NHPh)_4$, is produced; it is amorphous, melts and decomposes at 303°, and is insoluble in water.

Acetylacetonearabinamine, $CH_2Ac{\cdot}CMe{:}N{\cdot}C_5H_{11}O_4$, obtained by condensing acetylacetone with the amine, forms flattened needles, melts at 160°, is insoluble in water, and slightly soluble in alcohol.

Benzylidenearabinamine, $C_5H_{11}O_4{\cdot}N{:}CHPh$, forms colourless, rectangular lamellæ, melts at 160—161°, and is readily soluble in water and alcohol.

When arabinamine is treated with carbon disulphide, there is formed *2-thiol-5-propyltrioloxazoline*,

$$\begin{array}{l} \phantom{SH\cdot{}}N{\cdot}CH_2 \\ \phantom{SH\cdot{}}\| \\ SH{\cdot}C\text{——}O \end{array}\!\!>CH{\cdot}[CH{\cdot}OH]_2{\cdot}CH_2{\cdot}OH\,;$$

this crystallises in prismatic needles, melts at 172·5°, is soluble in water, slightly so in alcohol, and furnishes a *di-silver* derivative insoluble in water and alcohol.

Xylamine, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}NH_2$, similarly prepared, is a viscous, colourless liquid with a taste at once caustic and sweet; it is very soluble in water and alcohol, and has $[\alpha]_D$ $-8{\cdot}5°$ without mutarotation. The *hydriodide* crystallises in prismatic needles, has $[\alpha]_D$ $-12{\cdot}3°$, and is soluble in water, but insoluble in alcohol.

T. A. H.

Tri-propylenediaminechromium Salts. PAUL PFEIFFER and M. HAIMANN (*Ber.*, 1903, 36, 1063—1069. Compare Abstr., 1902, i, 728). —Although ethylenediamine (en) and potassium chromithiocyanate, $K_3Cr(SCN)_6$, yield the compound $[Cr(en)_2(SCN)_2]SCN$, $\alpha\beta$-propylenediamine (pn) gives the substance $Cr(pn)_3(SCN)_3$. The latter can also be prepared from propylenediamine and pyridine chromichloride.

Tripropylenediaminechromium-iodide, $Cr(pn)_3I_3,H_2O$, is obtained as a yellow, crystalline precipitate on adding potassium iodide to the solution of the chloride prepared from propylenediamine and pyridine chromichloride, or of the thiocyanate prepared from potassium thiocyanochromium thiocyanate and propylenediamine; its solution is not changed by potassium hydroxide, but is rendered strongly alkaline by moist silver oxide, silver iodide being precipitated. Picric acid forms a yellow, explosive precipitate, and potassium permanganate a brown precipitate. Mol. weight determinations in aqueous solution show that the substance is largely dissociated.

Tri-propylenediaminechromium thiocyanate, $Cr(pn)_3(SCN)_3$, is prepared either from the iodide or directly from the potassium thiocyanochromium thiocyanate. It crystallises in small, lustrous needles insoluble in all organic media except pyridine; at 100—120°, it becomes red, but recovers its original colour on cooling. The mol. weight in aqueous solution shows that it is largely dissociated. The *hexacyanochromium* salt, $Cr(pn)_3[Cr(CN)_6]$, is prepared from the iodide and potassium chromicyanide, and forms a yellow, crystalline precipitate, insoluble in water and not decomposed by heating to 140°. The *hexacyanocobaltic* salt, $Cr(pn)_3,[Co(CN)_6]$, prepared from the iodide and potassium cobalticyanide, is a yellow, insoluble, crystalline precipitate. The *hexathiocyanochromic* salt, $Cr(pn)_3[Cr(SCN)_6]$, is an insoluble, brown, crystalline precipitate, which gives a red solution on prolonged boiling with water and becomes red on heating at 120°. K. J. P. O.

Action of Cyanogen Bromide on Methylene Bases. JULIUS VON BRAUN and E. RÖVER (*Ber.*, 1903, 36, 1196—1199).—Tetramethylmethylenediamine, $CH_2(NMe_2)_2$, reacts with an ethereal solution of cyanogen bromide yielding dimethylcyanamide, $CN\cdot NMe_2$, and a solid quaternary compound which, on exposure to the air, yields formaldehyde and dimethylamine hydrobromide. The primary products are probably dimethylcyanamide and methylene bromide, and the latter reacts with the tertiary diamine yielding a quaternary compound, $CH_2{<}{\substack{NMe_2Br\\NMe_2Br}}{>}CH_2$. Tetrapropylmethylenediamine, dipiperidylmethylenediamine, and tetrabenzylmethylenediamine react in exactly the same manner with cyanogen bromide.

Tetrabenzylmethylenediamine, $CH_2(NBz_2)_2$, melts at 97°, is soluble in most organic solvents, and on treatment with dry hydrogen chloride yields dibenzylamine hydrochloride. Tetrapropylmethylenediamine and methyl iodide react in cold dry ethereal solution yielding the *quaternary* salt, $CH_2(NPr_2MeI)_2$, melting at 96°; it forms a snow-white powder and with water yields formaldehyde. J. J. S.

Bases Derived from Hexamethylenetetramine. KARL HOCK (D.R.-P. 139394).—When the products of the addition of alkyl halogen compounds to hexamethylenetetramine are warmed with strong solutions of alkali hydroxides or carbonates, new oily bases are formed; these substances take up water to form hydrates, which are insoluble in ether, but may be dehydrated by solid potassium hydroxide, and then dissolve in ether and benzene. The new bases, which are probably alkylpentamethylenetetramines, yield additive products with iodoform, chloral, phenols, and tartaric, picric, quinic, and tannic acids; they also combine with alkyl haloids to form crystalline ammonium salts. When gently heated, they break up into trialkyltrimethylenetriamines, hexamethylenetetramine, and ammonia; $3XC_5H_{11}N_4 = 2C_6H_{12}N_4 + X_3(CH_2)_3N_3 + NH_3$. Among the decomposition products thus obtained are *trimethyltrimethylenetriamine*, an oil boiling at 160—164°, *triethyltrimethylenetriamine*, boiling at 200—210°, and *tribenzyltrimethylenetriamine*, boiling at 230—240°. C. H. D.

Ethanolamine. LUDWIG KNORR and PAUL RÖSSLER (*Ber.*, 1903, 36, 1278—1283).—*Ethanolbenzamide*, $OH\cdot CH_2\cdot CH_2\cdot NHBz$, the first product of benzoylating ethanolamine by the Schotten-Baumann method, separates from ether as an oil which slowly solidifies and melts at about 58°. *Diethanoloxamide*, $C_2O_2(NH\cdot CH_2\cdot CH_2\cdot OH)_2$, from ethanolamine and ethyl oxalate, crystallises from alcohol and melts at 167—168°. *Ethanolbenzenesulphonamide*, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot SO_2Ph$, is an oil which boils with slight decomposition at 280° under 15 mm. pressure; the *sodium* salt forms a thick, crystalline paste. *Phenylethanolcarbamide*, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot NHPh$, crystallises from alcohol in flakes and melts at 122—123°; the *phenylurethane*,

$$NHPh\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot NHPh,$$

of the preceding compound forms white needles and melts at 195°. *Phenylethanolthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot CH_2\cdot OH$, crystallises from alcohol and melts at 138°. Cyanic acid converts the base into the compound $\begin{matrix}CH_2-O\\ | \quad\ \\ CH_2\cdot NH\end{matrix}\!>CO$, and carbon disulphide gives the compound $\begin{matrix}CH_2\cdot S\\ | \quad\ \\ CH_2\cdot N\end{matrix}\!\geqslant C\cdot SH$. Acetylacetone combines with ethanolamine to form a *compound*, $C_7H_{13}O_2N$, which crystallises from ether in white needles, melts at 78°, and probably has the formula

$$\begin{matrix}CH_2-O\\ | \quad\ \\ CH_2\cdot NH\end{matrix}\!>CMe\cdot CH_2Ac \text{ or } OH\cdot CH_2\cdot CH_2\cdot N\!:\!CMe\cdot CH_2Ac.$$

Ethyl acetoacetate gives a similar *compound*, $C_8H_{15}O_3N$, which crystallises from ether and melts at 31—32°. T. M. L.

Synthesis of Derivatives of Polypeptides. EMIL FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 387—400. Compare Abstr., 1901, i, 675, and 1902, i, 350).—The ordinary amino-acids are only convertible into the corresponding acid chlorides by means of thionyl chloride after the amino-group has been protected by the introduction of the carbethoxy-radicle. These acid chlorides combine easily with glycylglycine esters and similar compounds to form chains

of amino-acids joined together by an anhydride linking. Such are termed *polypeptides*, and are of considerable importance in view of the fact that careful partial hydrolysis of silk-fibroin yields a glycinealanine compound of this nature (E. Fischer, *Chem. Zeit.*, 1902, 26, 939).

Glycylglycinecarboxylic acid, $CO_2H\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, on alkylation with alcoholic hydrogen chloride, yields a neutral *β-ester* melting at 148—150° (corr.), isomeric with the known α-ethylglycylglycinecarboxylate melting at 87°. The β-ester is insoluble in ether and only sparingly so in benzene; on hydrolysis with sodium hydroxide, the dicarboxylic acid is regained. When left in contact with anhydrous liquid ammonia, it goes into solution readily, forming *β-carbaminoglycylglycineamide*, $C_5H_{10}O_3N_4$, which becomes brown at 230° and melts and decomposes at about 246° (corr.). The aqueous solution is sweet and gives a blue colour with copper salts. The platinichloride forms minute, yellow, six-sided plates. *α-Carbaminoglycylglycineamide*, $NH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH_2$, is obtained in a similar manner from the α-ester and crystallises in small, oblique prisms which melt and decompose at 210° (corr.) and give a bluish-violet colour with alkali and copper salts.

The cause of this isomerism is unknown; it is perhaps similar to that of the monomethyluric acids (Fischer and Ach).

The *chloride* of ethylhydrogenglycylglycinecarboxylate,

$$CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot COCl,$$

is obtained as an amorphous, red mass by the action of thionyl chloride on the glycine compound. When dissolved in chloroform and added to a cold solution of glycine ester, combination readily takes place with formation of *ethyl diglycylglycinecarboxylate*, $CO_2Et\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2Et$. This crystallises from water in spherical aggregates of microscopic needles melting at 163—164° (corr.); with alkali and copper salts, a distinctly reddish-violet coloration is produced. The same compound is also formed by the interaction of the chloride of ethyl glycinecarboxylate and glycylglycine-ester. Hydrolysed with a small quantity of sodium hydroxide, *ethyl hydrogen diglycylglycinecarboxylate*,

$$CO_2Et\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H,$$

is formed. This is soluble in less than 3 parts of hot water and crystallises in microscopic needles or thin plates, which sinter at 200° and melt at 212—214° (corr.). The aqueous solution is acid, dissolves copper oxide on boiling, and gives a dark violet-blue biuret reaction. The silver salt consists of minute, concentrically aggregated needles. When somewhat more than 2 mols. of alkali are used, *diglycylglycinecarboxylic acid*, $CO_2H\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H$, is formed on hydrolysis. This crystallises in oblique plates, melts and decomposes at 210°, and is sparingly soluble in alcohol. The aqueous solution is very acid and dissolves copper oxide with a green coloration on boiling.

Ethyl diglycylglycineamidecarboxylate, $CO_2Et\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH_2$, is prepared by the action of liquid anhydrous ammonia on the ester. It melts at 235° (corr.), crystallises from water in prisms, and gives a reddish-violet biuret coloration.

Diglycylglycineamidecarboxylic acid is formed on careful hydrolysis of the foregoing substance. It crystallises from water in small, oblique prisms which melt and decompose at 230—234° (corr.).

The esterification of diglycylglycinecarboxylic acid gives rise to a case of isomerism similar to that previously quoted; the new *β-ethyl diglycylglycinecarboxylate* crystallises in badly-defined plates, is more easily soluble in most solvents, and gives a pure blue coloration with alkali and copper salts. It melts at 148—150° (corr.), 12° lower than the α-isomeride.

Ethyl triglycylglycinecarboxylate,

$$CO_2Et\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2Et,$$

is sparingly soluble in water, from which it crystallises in oblique prisms melting at 235—236° (corr.). Liquid anhydrous ammonia converts it into *ethyl triglycylglycineamidecarboxylate*,

$$CO_2Et\cdot[NH\cdot CH_2\cdot CO]_4\cdot NH_2,$$

which melts and decomposes at 275° (corr.) and gives a reddish-violet biuret reaction. On hydrolysis, it forms *triglycylglycinecarboxylic acid*, $CO_2H\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2H$, which melts and decomposes at 235°. The aqueous solution is very acid and shows a bluish-violet biuret reaction.

β-Naphthalenesulphoglycylglycine (compare this vol., i, 24) can be obtained by the action of thionyl chloride on naphthalenesulphoglycine, and condensation of the chloride so formed with glycine ester. *Ethyl β-naphthalenesulphoglycylglycinecarboxylate* is formed as an intermediate product; this melts at 119—120°.

i-*β-Naphthalenesulphoglycylalanine*,

$$C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

is formed in a similar manner from naphthalenesulphoglycine, thionyl chloride, and *i*-alanine ester. It melts at 172—173° (corr.), is easily soluble in alcohol, and forms microscopic needles from water.

E. F. A.

Double and Triple Thiocyanates of Cæsium, Cobalt, and Silver. F. L. Shinn and Horace L. Wells (*Amer. Chem. J.*, 1903, 29, 474—478. Compare this vol., i, 154).—*Cæsium cobalt thiocyanate*, $Cs_2Co(CNS)_4,2H_2O$, corresponds in type with the magnesium and zinc cæsium thiocyanates previously described; it forms deep blue crystals, and when dehydrated melts at about 170°. *Cobalt silver thiocyanate*, $CoAg(CNS)_3,2H_2O$, does not correspond in type with other bivalent, metal-silver thiocyanates; it forms brilliant deep blue crystals which, when dehydrated, change to dark green. *Cæsium cobalt silver thiocyanate*, $Cs_2CoAg_2(CNS)_6,2H_2O$, corresponds with other triple thiocyanates; it crystallises in bright pink plates. The anhydrous salt is dark green and melts at about 180°. A. McK.

Cobaltous and Cobaltic Thiocyanogen Compounds. Julius Sand (*Ber.*, 1903, 36, 1436—1447).—*Cobaltotetrammine thiocyanate*, $Co(CNS)_2(NH_3)_4$, prepared by the action of ammonia on cobaltous ammonium thiocyanate, $Co(NH_4)_2(CNS)_4$, forms rose-red needles; the oxycobaltic *compound*, $O_2[Co(NH_3)_5(CNS)_2]_2$, is formed as a bye-product. By the action of iodine on the thiocyanate, there are produced

cobaltiisothiocyanopentammine iodide, $Co(CNS)(NH_3)_5I_2$, and *cobaltidithiocyanotetramminoiodide*, $Co(CNS)_2(NH_3)_4I_2$.

a-Cobaltotetrapyridine thiocyanate, $Co(CNS)_2(C_5H_5N)_4$, from cobaltoammonium thiocyanate and pyridine, forms beautiful, glistening, well-developed, peach-coloured prisms. The isomeric *β-compound*, prepared by heating this substance with alcohol and iodine, forms glistening, brown, ill-defined crystals. *Cobaltodipyridine thiocyanate*,

$$Co(C_5H_5N)_2(CNS)_2,$$

prepared by heating either of these isomerides in a boiling alcoholic solution or alone at 200°, separates from alcohol in dark violet-brown crystals and melts at 220° to a blue liquid.

Cobaltodianiline thiocyanate, $Co(NH_2Ph)_2(CNS)_2$, crystallises from boiling water in dark reddish-violet crystals and melts at 251° to a blue liquid.

Cobaltohexaphenylhydrazine thiocyanate, $Co(N_2H_3Ph)_6(CNS)_2$, forms rose-red, minute needles. T. M. L.

Metallic Derivatives of Thiocarbamide. VOLKMAR KOHLSCHÜTTER (*Ber.*, 1903, 36, 1151—1157. Compare Rosenheim and Loewenstamm, this vol, i, 325).—*Cuprotrithiocarbamide oxalate*, $[Cu(CSN_2H_4)_3]_2C_2O_4,7H_2O$, forms lustrous leaflets.

On adding potassium nitrate to a dilute solution of cuprotrithiocarbamide chloride, the sparingly soluble crystalline *nitrate*,

$$[Cu(H_2O)(CSN_2H_4)_2]NO_3,$$

is obtained; it melts at 100° and is formed by the replacement of CSN_2H_4 by H_2O in the original molecule. This substance yields a series of well-defined salts, including the sulphate,

$$[Cu(CSN_2H_4)_3]SO_4[Cu(H_2O)(CSN_2H_4)_2],H_2O,$$

described by Rosenheim and Loewenstamm (*loc. cit.*). If potassium nitrate be added to a more concentrated solution of the chloride, the *salt*, $Cu_2[(CSN_2H_4)_3][(CSN_2H_4)_2(H_2O)](NO_3)_2$, separates on further evaporation; it is easily soluble in water, melts at 86—88°, and forms spherular aggregates of prismatic needles. The *compound*,

$$Cu_3(CSN_2H_4)_7(H_2O)_2(NO_3)_3,$$

is obtained by dissolving the precipitate given by the chloride with nitric acid in 80 per cent. alcohol and precipitating with ether; it crystallises in slender, lustrous leaflets and melts at 96°.

Two *salts* of the formula $Hg(CN)_2(CSN_2H_4),\frac{1}{2}H_2O$ exist. One crystallises in small, well-formed, rhombic plates and is probably $[Hg(CSN_2H_4)_2(H_2O)](CN)_4Hg$; the other forms slender, silky scales and is perhaps $[Hg(CSN_2H_4)(H_2O)](CN)_4Hg(CSN_2H_4)$. The second differs from the first in being soluble in aqueous potassium chloride and corresponds with the cupro-salts already described.

The main part of the paper deals with the theoretical relationship between the salts. W. A. D.

Quantitative Formation of Carbamide from Uric Acid. E. RICHTER (*J. pr. Chem.*, 1903, [ii], 67, 274—280. Compare Abstr., 1902, ii, 632; Jolles, Abstr., 1900, ii, 450; 1902, i, 86; Falta, Abstr., 1901, ii, 705).—The author again confirms the accuracy of Jolles' method, which differs in several important points from that of Falta.

G. Y.

Methyleneaminoacetonitrile. AUGUST KLAGES (*Ber.*, 1903, 36, 1506—1512. Compare Jay and Curtius, Abstr., 1894, i, 162).—A 60 per cent. yield of this nitrile is obtained by mixing 1 kilo. of formaldehyde and 360 grams of ammonium chloride, cooling to 5°, and then, while stirring vigorously, adding, in the course of 3 hours, 440 grams of potassium cyanide dissolved in 600 c.c. of water. During the latter half of the operation, 250 c.c. of acetic acid are also run in. The methyleneaminoacetonitrile, $(CH_2{:}N{\cdot}CH_2{\cdot}CN)_2$, separates as a crystalline mass and is removed by filtration. By using sulphurous instead of acetic acid, the isomeride melting at 86° is obtained.

Alcoholic hydrogen chloride converts methyleneaminoacetonitrile into glycine ester hydrochloride. Yields of 90 per cent. are obtained by heating on the water-bath for an hour, filtering from ammonium chloride, and allowing to crystallise. If, however, after filtration the alcoholic solution is evaporated over a flame, only little glycine ester is formed, and a new substance, the tetrahydrochloride of an *amino-acid ester*, $C_{17}H_{40}O_{13}N_4,4HCl$, melting at 235° is obtained. This is hydrolysed by water to the hydrochloride of the *acid*, $C_9H_{16}O_9N_4,4HCl$, melting at 156°. The free acid, obtained by decomposition of the copper salt with hydrogen sulphide, forms colourless crystals having an acid taste, easily soluble in water, but insoluble in alcohol and ether; it melts at 229°. Alcoholic hydrochloric acid reconverts this into the tetraethyl ester, which can also be prepared synthetically by heating together methylal, glycine ester hydrochloride, and alcoholic hydrogen chloride.

Sodium nitrite in aqueous acid solution converts either of these compounds into a tetrabasic *acid*, $C_9H_{14}O_{12}N_4$. This melts at 149°, decomposes carbonates, and forms well-characterised metallic salts.

Alcoholic sulphuric acid forms less complicated products from methyleneaminoacetonitrile.

Aminoacetonitrile hydrogen sulphate, $NH_2{\cdot}CH_2{\cdot}CN,H_2SO_4$, forms colourless, glistening plates, easily soluble in water, and melting at 101° to a clear liquid.

Aminoacetonitrile sulphate, $(NH_2{\cdot}CH_2{\cdot}CN)_2,H_2SO_4$, crystallises from dilute alcohol in long, flat prisms which decompose at 165°.

Aminoacetonitrile picrate, $NH_2{\cdot}CH_2{\cdot}CN,C_6H_3O_7N_3$, crystallises from hot water in long, intensely yellow needles, which begin to decompose at 165°, blacken at 185°, and sinter at about 190°. E. F. A.

Abnormal Compounds of Nickel. KARL A. HOFMANN and F. HÖCHTLEN (*Ber.*, 1903, 36, 1149—1151).—From a cold aqueous solution of nickel sulphate, potassium cyanide and ammonia, steel-blue leaflets of *nickel cyanide*, $Ni(CN)_2,4H_2O$, separate after several days; on carefully adding acetic acid and subsequently benzene, a powdery, bluish-white precipitate of the *compound*, $Ni(CN)_2,NH_3,C_6H_6$, is obtained. The benzene is not removed by drying or by washing with alcohol and ether, but is liberated by mineral acids or alkalis, which decompose the complex; it is not present as benzene of crystallisation, for it still occurs when the salt is obtained amorphous.

Aniline gives a similar *compound*, $Ni(CN)_2,NH_3,NH_2Ph$, as a

granular, violet-white precipitate, and phenol, the analogous *derivative*, $Ni(CN)_2,NH_3,PhOH,H_2O$. W. A. D.

Monomethyl-tin Compounds. PAUL PFEIFFER and R. LEHNARDT (*Ber.*, 1903, 36, 1054—1061. Compare Abstr., 1902, i, 749).—On keeping a homogeneous mixture of methyl iodide, stannous chloride, and potassium hydroxide in dilute alcohol for a day at the ordinary temperature and then removing the hydroxide with carbon dioxide, a white powder, $CH_3\cdot SnO\cdot OH$ (for which the name *methylstannonic acid* is suggested), separates on evaporating the alcohol. If the alcohol is evaporated before the alkali is neutralised by carbon dioxide, a mixture of dimethylstannic oxide, $SnMe_2O$, and methylstannonic acid is formed, which is converted into bromides by treatment with hydrobromic acid; the latter are repeatedly precipitated with hydrobromic acid, when pure tindimethyl bromide, $SnMe_2Br_2$ (m. p. 74°), is obtained. On treating the mixture of oxides with hydriodic acid, the corresponding iodides are produced and separated by repeated precipitation with hydriodic acid, when the pure *tinmethyl iodide*, $SnMeI_3$, melting at 86°, is obtained. It crystallises from alcohol in long, flattened, yellow needles, is volatile with steam, is slowly hydrolysed by water, is reconverted into methylstannonic acid by ammonia, and transformed into the corresponding bromide (m. p. 53°) by hydrobromic acid.

Tinmethyl bromide, $SnMeBr_3$, is prepared by heating methylstannonic acid with fuming hydrobromic acid, and crystallises in silky needles melting at 53°; it is reconverted into methylstannonic acid by ammonia, and with hydrogen sulphide yields a white powder, soluble in ammonium sulphide, which is probably methylthiostannonic acid, $SnMeS\cdot SH$.

Methylstannonic acid is best prepared in a pure state by the action of ammonia on the bromide or iodide; it is an odourless, white powder, insoluble in water, sodium carbonate, or organic solvents, but soluble in alkali hydroxides, mineral acids, or acetic or tartaric acid. When boiled with 15 per cent. potassium hydroxide, it is converted into tindimethyl oxide, which yields an iodide with hydriodic acid. The latter forms with pyridine, in which it is soluble, a colourless additive product melting at 145° (Compare Cahours, *Annalen*, 1860, 114, 367). K. J. P. O.

Aluminium Compounds Exerting a Ferment Action. GABRIEL GUSTAVSON (*Compt. rend.*, 1903, 136, 1065—1067).—The liquid compounds produced by the action of alkyl halides on aluminium chloride or bromide (Abstr., 1886, 999) form unstable additive products with aromatic hydrocarbons, which undergo alkylation when treated with alkyl halides. Thus, by the action of ethyl bromide on aluminium chloride the compound Al_2Cl_6,C_8H_{16} is formed; this combines with 6 mols. of benzene forming the additive product $Al_2Cl_6,C_8H_{16},6C_6H_6$, which is dissociated into its generators by the application of heat or by washing with light petroleum, and reacts with ethyl bromide evolving hydrogen bromide and forming a new additive product in

which benzene is replaced by triethylbenzene and from which this is produced by the action of heat or by addition of light petroleum, the compound Al_2Cl_6,C_8H_{16} being simultaneously regenerated. In these, the latter reaction behaves like an enzyme.

The compound $Al_2Cl_6,C_6H_3Et_3$, exerting a similar ferment action, is produced when aluminium chloride (1 part), ethyl chloride (1 part), and benzene (2 parts) are mixed together. It is a viscous, yellow liquid, which boils and partially dissociates at 135—140° under 15 mm. pressure and is decomposed by water forming a *hydrocarbon* of the formula $C_6H_3Et_3$, which boils at 210—213° and furnishes a *tribromo*-derivative, which melts at 104—105°. This "ferment" combines with 6 mols. of benzene, 5 mols. of toluene, 4 mols. of *m*-xylene, 3 mols. of mesitylene, or 1 mol. of triethylbenzene, forming liquids which react with alkyl haloids, furnishing hydrogen bromide and alkylbenzenes, the compound $Al_2Cl_6,C_6H_3Et_3$ being regenerated in each case. T. A. H.

Addition of Bromine to Phenylbutadiene. C. N. Riiber (*Ber.*, 1903, 36, 1404—1407).—*Phenylbutadiene dibromide*,

$$CHPhBr·CH:CH·CH_2Br,$$

obtained by adding bromine dissolved in chloroform to a well-cooled solution of phenylbutadiene in the same solvent, crystallises from chloroform or carbon disulphide in large, slightly yellow pyramids and melts at 94°; by zinc methyl in absolute ether at 100°, it is converted into *dimethylbutenylbenzene*, CHMePh·CH:CHEt, which boils at 84° under 10 mm. pressure, and on oxidation with potassium permanganate in acetone solution gives hydratropic, propionic, and atrolactic acids. *Diethylbutenylbenzene*, $CHEtPh·CH:CH·CH_2Et$, obtained similarly by using zinc ethyl, boils at 104° under 8 mm. pressure and gives butyric and phenylbutyric acids on oxidation.

From the mother liquors of the dibromide, small quantities of two *tetrabromides*, $C_{10}H_{10}Br_4$, can be isolated; one of these, melting at 151°, is already known, and the other crystallises from light petroleum in large needles and melts at 76°. W. A. D.

Replacement of Bromine by Chlorine in the Benzene Ring. Alexander Eibner (*Ber.*, 1903, 36, 1229—1231).—Chlorine is able to displace bromine in bromobenzene, the reaction being accelerated by moisture and sunlight. The bromobenzene was saturated with chlorine seven times and was kept for 24 hours and washed with alkali after each saturation. On subsequent distillation, it yielded fractions boiling at 128—145°, 145—165°, 165—210°, 210—260°, and a black residue. From these fractions, chlorobenzene, *p*-dichlorobenzene, and tetrachlorobenzene, melting at 137°, were isolated. J. J. S.

Separation of *o*- and *p*-Chloronitrobenzenes. Leo Marckwald (D.R.-P. 137847).—On cooling the product of the nitration of chlorobenzene to 16°, *p*-chloronitrobenzene crystallises out, and on further cooling a eutectic mixture of about 21 parts of the *ortho*- and 10

parts of the *para*-isomeride is obtained. This, or any mixture of similar composition, may be separated into its constituents by extraction with a quantity of dilute ethyl or methyl alcohol insufficient for complete solution at a temperature above the melting point of the mixture. More *o*-chloronitrobenzene is extracted than corresponds with the eutectic composition. On cooling the residual mixture to 16°, a further quantity of the *para*-compound crystallises, and by distilling off the alcohol from the extract and cooling, crystals of the pure *ortho*-compound separate. The process may be repeated on the residual mixture.

C. H. D.

Chloro- and Bromo-cinnamylidene Chlorides. ERNEST CHARON and EDGAR DUGOUJON (*Compt. rend.*, 1903, **136**, 1072—1074. Compare Abstr., 1899, i, 469, and this vol., i, 240).—α-Bromocinnamaldehyde behaves as a saturated substance towards halogens, whilst α-chlorocinnamaldehyde combines with chlorine and bromine forming respectively trichloro- and chlorodibromo-cinnamaldehydes. These are viscous oils, furnishing crystalline hydrates, which dissociate when kept under reduced pressure over sulphuric acid, and are oxidised respectively by chromic acid to α-chloro-αβ-dibromophenylpropionic acid, $CHPhBr \cdot CClBr \cdot CO_2H$ (Forrer, *Ber.*, 1883, **16**, 855), and *ααβ-trichlorophenylpropionic acid*, $CHPhCl \cdot CCl_2 \cdot CO_2H$, which melts at 112°.

α-Chlorocinnamylidene chloride, $CHPh:CCl \cdot CHCl_2$, obtained by the action of phosphorus pentachloride on α-chlorocinnamaldehyde, crystallises in nacreous leaflets, melts at 47°, and boils at 155° under 30 mm. pressure; it is decomposed by water, forming α-chlorocinnamaldehyde and hydrogen chloride.

α-Bromocinnamylidene chloride, similarly prepared, melts at 55°, boils at 167—168° under 305 mm. pressure, and is not decomposed by water even at 100°.

These results indicate that the attachment of a halogen atom to an ethylenic carbon in an alkyl chloride increases the stability of the latter.

T. A. H.

Stilbene from Phenylnitromethane. WILHELM WISLICENUS and ANTON ENDRES (*Ber.*, 1903, **36**, 1194—1195).—Phenylnitroacetonitrile (*iso*nitrobenzyl cyanide; Abstr., 1902, i, 541) is readily transformed into stilbene according to the equation: $2CN \cdot CPh:NO \cdot ONa + 4NaOH + 2H_2O = CHPh:CHPh + 2Na_2CO_3 + 2NH_3 + 2NaNO_2$, when its sodium derivative is heated with slightly less than the theoretical amount of 10 per cent. sodium hydroxide for 8—10 hours at 180—200°.

Stilbene is also formed when phenylnitromethane is heated with the calculated amount of 10 per cent. alkali at 160°.

J. J. S.

Action of Zinc on Triphenylchloromethane. MOSES GOMBERG (*Amer. Chem. J.*, 1903, **29**, 364—371).—A reply to Norris and Culver (this vol., i, 333).

E. G.

Tetraphenylmethane. Moses Gomberg and H. W. Berger (*Ber.*, 1903, **36**, 1088—1092. Compare Abstr., 1897, i, 623, and Ullmann and Münzhuber, this vol., i, 245).—Triphenylmethanehydrazobenzene is best obtained by the reaction between chlorotriphenylmethane and phenylhydrazine in absolute ethereal solution, and is most readily oxidised to triphenylmethaneazobenzene by means of nitrous vapours. The decomposition of the latter substance by heat is effected by warming a mixture with three to four parts of sand at 100° in a current of carbon dioxide, the resulting hydrocarbon being extracted with benzene. The yield varies from 2 to 5 per cent., but in one instance amounted to 20 per cent. After repeated crystallisation from benzene, the hydrocarbon is obtained colourless and then melts at 285°. On nitration with cold fuming nitric acid, a trinitrotetraphenylmethane is formed, which, on crystallisation from ethyl acetate, forms faintly yellow needles melting at about 330° and giving, on reduction with zinc dust, a magenta solution which appears to have the same absorption spectrum as the triphenylmethane dye. G. D. L.

Preparation of Acyl Derivatives of Aromatic Bases and of Anhydrous Glycerol. Oskar Liebreich (D.R.-P. 136274).—Aromatic bases, such as aniline, naphthylamines, diamines, or their monoalkyl derivatives, are heated under pressure with animal or vegetable fats or oils at about 200°. The anilides, &c., of the fatty acids are formed, together with anhydrous glycerol, which may be separated by distillation. C. H. D.

A Practical Modification of the Technical "Baking" Method of Preparing Sulphonic Acids of Aromatic Bases. Alfred Junghahn (*Chem. Centr.*, 1903, i, 572; from *Chem. Ind.*, **26**, 57—59).—The sulphonic acids of aromatic bases are prepared on the large scale by heating the acid sulphates of the bases in shallow trays at 200—230° for a long time. Attempts to prepare 4-*m*-xylidine-5-sulphonic acid from the corresponding sulphate by this means, however, failed (compare this vol., i, 22), and Deumelandt's method (*Zeit. Chem.*, 1866, 22) yielded only 4-*m*-xylidine-6-sulphonic acid; the barium salt of this acid crystallises in slender needles and is readily soluble in water. The 5-sulphonic acid may be prepared by heating the corresponding sulphate at 160°, then raising the temperature to 220°, and at the same time passing a stream of carbon dioxide or air through the mass. After maintaining this temperâture for about an hour and rapidly stirring, the almost pure sulphonic acid is obtained in the form of a dry powder. The oxidation products present in the acids prepared by the technical process cannot therefore be due to the action of the oxygen of the air, but rather to that of the sulphuric acid. The action of sulphuric acid at a high temperature, in fact, tends to remove the sulphonic acid group from 4-*m*-xylidinesulphonic acid (compare Bender, Abstr., 1889, 717). In a similar manner, by using a stream of gas or air, aniline sulphate is converted into sulphanilic acid, and *p*-xylidine sulphate into 1 : 4 : 2-xylidine-5-sulphonic acid (compare Noelting, Witt, and Forel, Abstr., 1886, 57); the latter, on oxidation with chromic acid, forms *p*-xyloquinone. The sulphonic

acids of dimethylaniline and of bases which are not readily sulphonated in the ordinary way may be easily prepared by employing a stream of carbon dioxide, and at the same time removing the gas in contact with the mass by means of a vacuum pump. The dimethylanilinesulphonic acid obtained by this method appears to be identical with Bamberger and Tschirner's *para*-acid (Abstr., 1899, i, 682), although it decomposes at the same temperature as the *meta*-acid (265—266°), and also crystallises in a similar form. When fused with sodium hydroxide, however, it yields only traces of a substance resembling a phenol, whilst the *meta*-acid, under like conditions, forms a considerable quantity of *m*-dimethylaminophenol.

In the technical process, 4-*m*-xylidine-5-sulphonic acid is probably formed directly from the sulphate at 200—210° without the intervention of intermediate products (compare Bamberger and Kunz, Abstr., 1898, i, 31), for neither the presence of 4-*m*-xylenesulphonamic acid nor of 4-*m*-xylene-6-sulphonic acid could be detected. On the other hand, when 4-*m*-xylenesulphonamic acid is heated at 200—210°, it is almost instantaneously converted into 4-*m*-xylene-5-sulphonic acid. E. W. W.

[New Bases from Acetylated Aromatic Amines.] ERNST SILBERSTEIN (D.R.-P. 137121).—When acetanilide and its homologues react with phosphorus oxychloride, there are formed, in addition to the amidines, a series of new bases which differ in composition from the original material by the loss of the elements of water. The reacting substances are heated together for several hours on a water-bath and poured into water. The new bases differ in their properties from Wallach's base (Abstr., 1877, i, 187) and from flavaniline. In their formation, 2 mols. of the acetyl compound lose 2 mols. of water, whilst only one is lost in the production of amidines.

The *hydrochloride* of the base from acetanilide, $C_{16}H_{14}N_2,HCl$, crystallises from alcohol in bright yellow needles, sinters at 170°, and melts at 266°, and is soluble in hot water; the *base* forms colourless needles melting at 156° and dissolving with difficulty in water, but readily soluble in alcohol.

The *hydrochloride* of the base from phenacetin forms yellow needles melting at 265°; the colourless *base* melts at 220°. C. H. D.

Addition of Aniline to Monobasic Unsaturated Acids and their Anilides. WILHELM AUTENRIETH and C. PRETZELL (*Ber.*, 1903, 36, 1262).—*β-Anilinopropionanilide*, $NHPh\cdot CH_2\cdot CH_2\cdot CO\cdot NHPh$, prepared by heating acrylic acid and aniline at 180—190°, crystallises from alcohol in pearly flakes, melts at 92—93°, and is almost insoluble in water; its constitution was established by preparing it from β-anilinopropionic acid and from β-iodopropionic acid. The *hydrochloride* crystallises from hot 20 per cent. hydrochloric acid in glistening prisms and melts at 173—174°.

β-Anilinobutyranilide, $NHPh\cdot CHMe\cdot CH_2\cdot CO\cdot NHPh$, prepared in a similar way from aniline and crotonic acid, crotonanilide, or vinylacetic acid, crystallises from alcohol in minute needles and melts at 93°; the hydrochloride has been described by Balbiano (Abstr., 1880, 541).

Methylacrylanilide, $CH_2:CMe\cdot CO\cdot NHPh$, crystallises in glistening flakes and melts at 87°; the *dibromide*, $CH_2Br\cdot CMeBr\cdot CO\cdot NHPh$, crystallises from alcohol in minute needles and melts at 128°. *β-Anilino*iso*butyranilide*, $NHPh\cdot CH_2\cdot CHMe\cdot CO\cdot NHPh$, has already been described by Bischoff (Abstr., 1891, 828), but was incorrectly formulated as methacrylanilide; the *dibromo*-derivative, $C_{16}H_{16}ON_2Br_2$, melts at 152°. A description is given of a slightly modified method of preparing methylacrylic acid from citraconic anhydride. T. M. L.

Preparation of Anilinoacetonitrile and its Derivatives FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 138098).—Glycollonitrile reacts with aniline and its homologues or derivatives to form condensation products similar to anilinoacetonitrile,

$$OH\cdot CH_2\cdot CN + NH_2Ph = NHPh\cdot CH_2\cdot CN + H_2O.$$

The reaction takes place slowly at the ordinary temperature in aqueous or alcoholic solution, but rapidly on heating. C. H. D.

New Reduction Product of Dinitrostilbenedisulphonic Acid. Nitroaminostilbenedisulphonic acid. ANDRÉ WAHL (*Bull. Soc. chim.*, 1903, [iii], 29, 345—350).—When sodium dinitrostilbenedisulphonate (Green and Wahl, Abstr., 1898, i, 700) is reduced in aqueous solution by sodium sulphide, there is formed *sodium hydrogen nitroaminostilbenedisulphonate*, $C_{14}H_{11}O_8N_2S_2Na$, which crystallises in small, yellow needles and is slightly soluble in water. The normal salts are very soluble in water and highly coloured. The acid salt does not react with hypochlorites, but is oxidised by permanganate to *p*-nitro-*o*-sulphobenzaldehyde and probably *p*-amino-*o*-sulphobenzaldehyde, though the latter could not be isolated. Zinc, in ammonium chloride solution, reduces it to the corresponding diaminostilbenedisulphonate. Sodium hydrogen nitroaminostilbenedisulphonate dyes silk and wool orange-yellow in an acid bath; it forms a *diazo*-derivative insoluble in acids, but soluble in alkalis. The azo-dyes derived from this base are non-substantive, and so differ from those obtained from diaminostilbenedisulphonic acid, in which the substantive character has been regarded as due to the ethylenic linking of stilbene. The author therefore agrees with Friedländer (*Chem. Zeit.*, 1902, 698) that the substantive nature of dyes of this type may be correlated with physical properties the relation of which to their constitution is so far unknown. T. A. H.

Acylhalogenamine Derivatives and the Beckmann Rearrangement. EDWIN E. SLOSSON (*Amer. Chem. J.*, 1903, 29, 289—319. Compare Abstr., 1896, i, 216; Proc., 1900, 1—2; and Abstr., 1901, i, 462).—The Beckmann rearrangement, which takes place readily with the halogen amides, cannot be effected in the case of the acylalkylhalogenamines. It seems, therefore, that the hydrogen atom of the group $\cdot CO\cdot NH$ is necessary for the transformation to occur (compare Stieglitz, Abstr., 1897, i, 43; and this vol., i, 235).

Methyl phenylmethylcarbamate, $NPhMe\cdot CO_2Me$, obtained by the

action of methyl chlorocarbonate on methylaniline, is a light yellow oil which has a fishy odour, boils at 235°, and is easily soluble in ether or light petroleum.

Acetylbromoaminobenzene (acetylphenylbromoamine) crystallises in yellow flakes and melts at 94—95°. Benzoylchloroaminobenzene (benzoylphenylchloroamine) forms large, transparent crystals, melts at 81·5—82°, and is easily soluble in ether or alcohol. *p*-Chlorobenzoylaniline melts at 187—187·5°.

Formylchloroamino-p-*toluene* (*formyl*-p-*tolylchloroamine*),

$$CHO\cdot NCl\cdot C_6H_4Me,$$

crystallises from light petroleum, melts at 49—50°, and decomposes at 110°. *Formylbromoamino*-p-*toluene* (*formyl*-p-*tolylbromoamine*),

$$CHO\cdot NBr\cdot C_6H_4Me,$$

melts at 80° and is very unstable. *Formylchloroamino-α-naphthalene* (*formyl-α-naphthylchloroamine*), $CHO\cdot NCl\cdot C_{10}H_7$, melts at 63° and is unstable. The corresponding *β-naphthyl* compound melts at 75°. When an alcoholic solution of formyl-*β*-naphthylamine is added to a solution of potassium hypobromite, a yellow precipitate is produced, which, when crystallised from alcohol, melts at 164°; when this *substance* is heated with potassium hydroxide solution, a compound melting at 63° is formed, which is probably 1-bromo-2-aminonaphthalene. *Acetylchloroamino-α-naphthalene* (*acetyl-α-naphthylchloroamine*),

$$NClAc\cdot C_{10}H_7,$$

forms white crystals and melts at 75°.

Benzoylchloroaminoethane (*benzoylethylchloroamine*), $NClBz\cdot C_2H_5$, obtained by the action of chlorine water on ethylbenzamide, crystallises in white needles, melts at 53·5°, and is soluble in ether, alcohol, or hot water. *Ethylnitrobenzamide*, prepared by the action of *m*-nitrobenzoyl chloride on ethylamine, melts at 120°; attempts to convert it into the nitrogen chloride were unsuccessful. *Benzoylchloroaminomethane* (*benzoylmethylchloroamine*), $NClBz\cdot CH_3$, is a colourless oil, which does not solidify at −16°, and is much less stable than the corresponding ethyl compound. *iso*Amylacetamide is an oil which boils at 230—232°.

Ethyl chloroiminobenzoate (benzoylchloroiminoethyl ether; Stieglitz, Abstr., 1897, i, 44) does not react with potassium cyanide, and, when treated with zinc ethyl, yields benzonitrile and a small quantity of ethylamine. Ethyl chloroimino-*m*-nitrobenzoate crystallises in slender, white needles and melts at 61°; it is decomposed by heat with formation of *m*-nitrobenzamide and a small amount of ethyl *m*-nitrobenzoate. Ethyl bromoimino-*m*-nitrobenzoate crystallises in white needles, melts at 71°, and decomposes at 120—130°. Ethyl chloroimino-*β*-naphthoate crystallises in stellate groups of needles or plates, melts at 71°, decomposes at 185°, and is very soluble in ether; when it is heated with sodium methoxide or potassium cyanide, naphthonitrile is produced. Naphthonitrile is also obtained when ethyl chloroimino-*β*-naphthoate is treated with zinc ethyl, but there is no evidence of the formation of an amine. Ethyl bromoimino-*β*-naphthoate crystallises in white needles and melts at 76·5—77°. E. G.

Formation and Decomposition of Thiocarbamides. A. HUGERSHOFF (*Ber.*, 1903, 36, 1138—1142. Compare Kjellin, this vol., i, 287).—Phenyl-*o*-nitro-*p*-tolylthiocarbamide (Steudemann, Abstr., 1884, 307) melts at 143°, solidifies on further heating, and remelts at 169°. This behaviour is due to the formation of di-*o*-nitro-di-*p*-tolylthiocarbamide, a change also brought about by recrystallisation from alcohol or acetic acid.

Diphenylthiocarbamide and dinitroditolylthiocarbamide, when fused together, furnish phenylnitrotolylthiocarbamide, and, similarly, when a mixture of diphenylthiocarbamide and di-*o*-tolylthiocarbamide, in molecular quantities, is melted, or heated in alcoholic solution, there is formed phenyl-*o*-tolylthiocarbamide; but, on the other hand, when mixtures of di-*p*-tolylthiocarbamide with either diphenylthiocarbamide or di-*o*-tolylthiocarbamide are thus treated, no homogeneous product can be isolated from the product. T. A. H.

Dithiocarbamates derived from Secondary Aromatic Amines. GUSTAV HELLER [with FRIEDRICH MICHEL] (*J. pr. Chem.*, 1903, [ii], 67, 285—287. Compare Abstr., 1902, i, 444, and Delépine, Abstr., 1902, i, 702).—*Ethyl phenylmethyldithiocarbamate*, formed by the action of ethyl iodide on the ammonium salt, crystallises in leaflets or prisms and melts at 94·5—95·5°. Ammonium phenylethyldithiocarbamate crystallises in glistening leaflets, melts at 110°, and on acidification at 0° yields the *acid*, which crystallises in delicate needles and decomposes at the ordinary temperature into ethylaniline and carbon disulphide. The *methyl* ester crystallises in needles, melts at 52—53°, and is easily soluble in chloroform, ether, or light petroleum.

Ammonium phenylbenzyldithiocarbamate, $CH_2Ph{\cdot}NPh{\cdot}CS{\cdot}SNH_4$, crystallises from warm water and melts at 92·5—93°. The addition of ammonia and carbon disulphide to benzylaniline takes place less easily than to methyl- or ethyl-aniline; with diphenylamine, the addition does not take place. In aqueous solution, these ammonium dithiocarbamates decompose, slowly at the ordinary temperature, more quickly when heated, into ammonia, carbon disulphide, and the secondary aromatic amine. G. Y.

Action of Phosgene on *p*-Aminophenol. P. SCHÖNHERR (*J. pr. Chem.*, 1903, [ii], 67, 339—341).—The action of phosgene on *p*-aminophenol in xylene solution at 210—220° leads to the formation of the *p*-hydroxyphenylcarbimidechlorocarbonate, $COCl{\cdot}O{\cdot}C_6H_4{\cdot}NCO$, which forms a white, waxy mass, melts at 36—37°, is easily soluble in ether or benzene, and has a colour resembling ethyl chlorocarbonate. When heated with phenol at 160°, it forms the *phenyl* ester of the *urethane*, $COCl{\cdot}O{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}OPh$, which crystallises in yellow, glistening leaflets and melts at 143—144°. With aniline, the carbimide forms *p*-hydroxydiphenylcarbamide phenylcarbamate (compare Fischer, Abstr., 1900, i, 418). With alcohol at 150°, the carbimide forms *p*-hydroxyphenylurethane. G. Y.

Aryl Thiocyanates and their Action on Thioacetic Acid and Ethyl Mercaptan. A. SPAHR (*Arch. Sci. phys. nat.*, 1903, [iv], 15, 336—337).—Aryl thiocyanates are best prepared by the action of

cyanogen chloride on lead mercaptides (*Ber.*, 1874, 7, 1753), this method giving better yields and purer products than that used by Anschütz (Abstr., 1889, 707).

o-*Tolyl thiocyanate* is a colourless liquid which boils at 170° under a pressure of 10 mm. and has a sp. gr. 1·1266 at 15°. p-*Tolyl thiocyanate* is a colourless liquid of pleasant odour.

p-*Chlorophenyl thiocyanate* forms white needles with a silky lustre, is soluble in alcohol, ether, and benzene, and boils at 31·8°. p-*Bromophenyl thiocyanate* resembles the foregoing and melts at 50·2°. p-*Nitrophenyl thiocyanate* is a faintly yellow solid, soluble in ether and alcohol, and melts at 124·2°.

Phenyl thiocyanate combines with thioacetic acid to form *phenyl acetyliminodithiolcarbonate*, NAc:C(SH)·SPh. This crystallises in yellow needles, melts at 146·4° to 146·6°, and forms with sodium a crystalline, deliquescent *derivative* which, when warmed, decomposes into sodium thiocyanate and *phenyl thioacetate*; the latter is a colourless liquid which boils at 220—221° and has a sp. gr. 1·127 at 15°.

Phenylacetyliminodithiolcarbonate may decompose in three ways: into phenyl mercaptan and acetylthiocarbimide, or phenyl thioacetate and thiocyanic acid, or into phenyl thiocyanate and thioacetic acid. With ethyl mercaptan, phenyl thiocyanate forms no additive product, but reacts to form ethyl, phenyl, and ethylphenyl disulphides, hydrogen cyanide, ammonia, and hydrogen being simultaneously produced.

T. A. H.

A New Di-iodophenol. P. Brenans (*Compt. rend.*, 1903, **136**, 1077—1079. Compare Abstr., 1901, i, 322, 643, and 1902, i, 280, 673).—3 : 4-*Di-iodo*-1-*nitrobenzene*, prepared by diazotising the corresponding iodonitroaniline in presence of potassium iodide, forms long, sulphur-yellow prisms, melts at 112·5°, and is identical with that prepared by Körner and Wender (Abstr., 1888, 1280). From this, by reduction with stannous chloride, 3 : 4-*di-iodoaniline*, crystallising in pale yellow leaflets, was prepared; it melts at 74·5° and is soluble in benzene, ether, and alcohol, less so in petroleum. The *benzoyl* derivative crystallises in colourless needles, melts at 174° (corr.), and is slightly soluble in benzene and light petroleum.

3 : 4-*Di-iodophenol*, obtained by diazotising the 3 : 4-di-iodoaniline, forms colourless needles, melts at 83°, and is soluble in organic solvents with the exception of light petroleum. The *benzoate* crystallises in colourless needles, melts at 123°, and is soluble in benzene, alcohol, and acetic acid.

T. A. H.

4-Choro-2-nitroanisole. Badische Anilin- and Soda-Fabrik (D.R.-P. 140133).—4-*Chloro*-2-*nitroanisole*, prepared by heating together molecular proportions of 2 : 5-dichloronitrobenzene and sodium hydroxide in methyl alcohol, crystallises from hot alcohol in small, flat, pale yellow prisms melting at 94—96°; it is very slightly soluble in cold alcohol, ether, or light petroleum; it differs in melting point from Reverdin's *p*-chloronitroanisole (Abstr., 1897, i, 28), and must be assumed to have the above constitution owing to its formation from

2 : 5-dichloronitrobenzene, the chlorine atom occupying the *o*-position with respect to the nitro-group being the more readily replaced.

C. H. D.

Separation of *p*- and *m*-Cresols. FIRMA RUD. RÜTGERS (D.R.-P 137584).—The commercial mixture of cresols is heated gently, and mixed with about a tenth part of dehydrated oxalic acid. On cooling, crystals of the *p*-tolyl oxalate separate, and are purified by draining and washing with benzene. The *m*-cresol is not esterified.

p-*Tolyl oxalate*, $C_6H_4(CH_3)O·CO·CO_2H$, forms colourless crystals which are fairly stable in air and sublime in leaflets. It is easily soluble in alcohol, ether, or glacial acetic acid, and insoluble in benzene. It is readily hydrolysed by water, and may be conveniently decomposed by heating with water and benzene or by distillation with steam. On heating in a melting point tube, the compound shrinks at 90°, becomes transparent at 99°, and melts with evolution of gas at 185—186°, this temperature approximating to the melting point of anhydrous oxalic acid.

C. H. D.

Aromatic Propylene Derivatives. II. *o*-Anethole. CARL HELL and H. BAUER (*Ber.*, 1903, 36, 1184—1192. Compare this vol., i, 242).—When *o*-anethole is brominated in chloroform solution, it gives not the dibromide, but *bromo-*o*-anethole dibromide*,

$$OMe·C_6H_3Br·CHBr·CHMeBr,$$

which crystallises from alcohol and light petroleum in slender, colourless needles, melts at 84—85°, and by boiling alcoholic sodium ethoxide (1 mol.) is converted into the *propenyl* compound,

$$OMe·C_6H_3Br·CH⁚CMeBr;$$

this is a bright yellow, odourless oil, which boils at 160—162° under 10 mm. pressure and with bromine gives *bromo-*o*-anethole tribromide*, $OMe·C_6H_3Br·CHBr·CMeBr_2$, crystallising from light petroleum in cubes and melting at 105—106°.

When bromo-*o*-anethole dibromide is boiled with an excess of alcoholic sodium ethoxide for 6 hours, it loses 2HBr and gives *bromo-*o*-anisylmethylacetylene*, $OMe·C_6H_3Br·C⋮CMe$, which boils at 148—149° under 10 mm. pressure, and with bromine yields not a tetrabromide, but the dibromide, $OMe·C_6H_3Br·CBr⁚CMeBr$, as a yellow, viscid oil.

*Dibromo-*o*-anethole dibromide*, $OMe·C_6H_2Br_2·CHBr·CHMeBr$, obtained by adding *o*-anethole to an excess of bromine, crystallises from alcohol or light petroleum in colourless cubes and is converted by 1 mol. of sodium ethoxide into *tribromomethoxypropenylbenzene*, $OMe·C_6H_2Br_2·CH⁚CMeBr$, which boils at 172—173° under 10 mm. pressure and absorbs bromine to form a liquid, *dibromo-*o*-anethole tribromide*, $OMe·C_6H_2Br_2·CHBr·CMeBr_2$. The action of an excess of sodium methoxide on dibromo-*o*-anethole dibromide converts it into *dibromo-*o*-anisylmethylacetylene*, $OMe·C_6H_2Br_2·C⋮CMe$, which boils at 165—166° under 10 mm. pressure; the *dibromide* of this is a viscid, colourless oil.

It is noteworthy that from *o*-anethole, derivatives corresponding with the compound $OMe·C_6H_4·CH(OEt)·CHMeBr$, derived from *p*-anethole, cannot be prepared; moreover, the bromides obtained from *o*-anethole

are not reactive with aniline and alcohol, like those of *p*-anethole (compare this vol., i, 242). W. A. D.

Conversion of β-Naphthylamine and its Derivatives into β-Naphthol and its Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 134401).—The naphthylamine derivatives are boiled with solutions of hydrogen sulphites, with or without the addition of sulphurous acid, until the reaction is complete (compare Abstr., 1901, i, 695, 699; 1902, i, 91, 366).

The use of an excess of the reagent favours the reaction. The sulphurous ester formed is hydrolysed by means of alkali, or in some cases by heating with mineral acids. The reaction takes place most readily with those derivatives of β-naphthylamine in which the 4-position is open. It may be applied to β-aminonaphthol and the naphthylenediamines, and also to their sulphonic acids. Thus, 6-amino-α-naphthol-3-sulphonic acid is converted into 2 : 5-dihydroxynaphthalene-7-sulphonic acid. C. H. D.

Functions of β-Naphtholaldaminic Bases. Mario Betti [with Andrea Torricelli] (*Gazzetta*, 1903, 33, i, 1—17).—The authors have studied the nature and transformations of several β-naphtholaldamines, $OH{\cdot}C_{10}H_6{\cdot}CRH{\cdot}NH_2$, which form a new series of bases possessing properties intermediate between those of the amines and amides. In general, they have a basic character rather more pronounced than that of the acid amides and, as regards the substitution of their typical hydrogen, resemble the alkylamines. Although they do not contain the $-CO{\cdot}NH_2$ group characteristic of the acid amides, they have many properties in common with the latter, notably that of decomposing with evolution of ammonia. The corresponding secondary bases, $OH{\cdot}C_{10}H_6{\cdot}CHR{\cdot}NHR$ (see Abstr., 1901, i, 81, 753, and 778) have no basic character.

β-Naphtholbenzylamine (aminobenzylidene-β-naphthol, see Abstr., 1901, i, 611) hydrochloride, when treated with 20 per cent. potassium hydroxide solution, yields 2 : 4-diphenyl-1 : 3-β-naphtho*iso*oxazine. *β-Naphtholbenzylamine picrate*, $C_{17}H_{15}ON,C_6H_3O(NO_2)_3$, forms orange-yellow crystals which melt and decompose at above 200°; the *platinichloride* and the *mercurichloride*, $C_{17}H_{15}ON,HCl,HgCl_2$, were prepared. *Monoacetyl-β-naphtholbenzylamine*, $C_{17}H_{13}O{\cdot}NHAc$, separates from a mixture of alcohol and acetic acid in minute, shining crystals melting at 236—237°; it is decomposed by boiling 20 per cent. potassium hydroxide solution but is stable towards dilute hydrochloric acid. The monoacetyl derivative may be obtained by treating the diacetyl compound (Abstr., 1901, i, 611) with 20 per cent. potassium hydroxide solution or by heating together β-naphthol (1 mol.), acetamide (1 mol.), and excess of benzaldehyde. The *monobenzoyl* derivative,

$$C_{17}H_{13}O{\cdot}NHBz,$$

crystallises from alcohol in silky needles melting at 225°.

*β-Naphthol*iso*valeralamine* [*β-naphthol*iso*amylamine*],

$$OH{\cdot}C_{10}H_6{\cdot}CH(C_4H_9){\cdot}NH_2,$$

obtained by the condensation of β-naphthol, *iso*valeraldehyde, and ammonia, crystallises from ether in very long, shining, white needles

melting at 114°; its benzene solution gives an intense reddish-violet coloration with ethereal ferric chloride solution. The *picrate* is deposited from alcohol in shining, yellow crystals which decompose without melting.

β-Naphtholfurfurylcarbinylamine, $OH\cdot C_{10}H_6\cdot CH(C_4H_3O)\cdot NH_2$, prepared by the interaction of β-naphthol, furfuraldehyde, and ammonia, forms almost white scales melting at 115°. The *hydrochloride* separates from alcohol in large, transparent crystals which exhibit a faint yellow-violet dichroism and turn brown at 100°, but do not melt even at 200°.

The condensation product of β-naphthol (1 mol.), salicylaldehyde (2 mols.), and ammonia, $C_{24}H_{19}O_3N$, melts at 162° and, when dissolved in benzene, gives an intense violet coloration with ethereal ferric chloride. With hydrochloric acid, it yields *β-naphtholsalicylideneamine* [*β-naphthol*-o-*hydroxybenzylamine*] *hydrochloride*,

$$OH\cdot C_{10}H_6\cdot CH(C_6H_4\cdot OH)\cdot NH_2,HCl,$$

which separates from alcohol acidified with hydrochloric acid in pale yellow, shining crystals. The free base could not be isolated.

T. H. P.

A New Synthesis of the Benzene Ring. FRITZ FICHTER and ERNST GRETHER (*Ber.*, 1903, 36, 1407—1411).—When cinnamaldehyde and sodium phenylsuccinate are heated with acetic anhydride at 130°, carbon dioxide is evolved and small quantities of *βε-diphenyl-βδ-pentadiene-α-carboxylic acid*, $CHPh\!:\!CH\cdot CH\!:\!CPh\cdot CH_2\cdot CO_2H$, formed; it crystallises from toluene in large, transparent plates containing solvent of crystallisation and melts at 140°. This substance is not the principal product of the action, but p-*diphenylphenol*,

$$CPh{<}\begin{matrix}CH\text{——}CH\\ C(OH)\!:\!CH\end{matrix}{>}CPh,$$

which is formed from it by the loss of $1H_2O$; the latter separates from benzene in radiating needles, from alcohol in thick, monosymmetric plates, melts at 194°, sublimes above 200°, its structure is indicated by the following facts. p-*Diphenylphenol acetate*, $C_{20}H_{16}O_2$, prepared by acetylation with acetic anhydride and sodium acetate, crystallises from alcohol in lustrous leaflets and melts at 144°; the corresponding *benzoate* forms small, interlacing needles and melts at 105°. The phenol is dissolved only by a great excess of highly concentrated aqueous sodium hydroxide, and is easily brominated in carbon tetrachloride solution, giving the *monobromo*-derivative, $CPh{<}\begin{matrix}CH\text{——}CBr\\ C(OH)\!:\!CH\end{matrix}{>}CPh$, which crystallises from light petroleum in colourless, crystalline, nodular aggregates, melts at 86°, and is not further attacked by bromine. With nitric acid in acetic acid solution, a *dinitrodiphenylphenol*, $CPh{<}\begin{matrix}CH\text{——}C(NO_2)\\ C(OH)\!:\!C(NO_2)\end{matrix}{>}CPh$, is obtained, which crystallises from alcohol in flat, yellow needles, melts at 193—194°, and is strongly acid; its *potassium* salt, $C_{18}H_{11}N_2O_5K$, forms bright yellow needles. The foregoing formula is given to the dinitro-compound because of the analogy it shows with picric acid and 2:4-dinitro-α-naphthol in readily dyeing silk and wool yellow.

p-Diphenylbenzene is obtained from *p*-diphenyldiphenol by distilling it with zinc dust. W. A. D.

Condensation of Dinitriles with Phenols. ERNST VON MEYER (*J. pr. Chem.*, 1903, [ii], 67, 342—343).—The action of hydrogen chloride on benzoacetodinitrile and resorcinol leads to the formation of 3-hydroxyflavone, which melts at 242—243° (compare Emilewicz and Kostanecki, Abstr., 1898, i, 369).

The action of sulphuric acid on dinitriles and resorcinol in glacial acetic acid leads to the formation of nitrogenous, fluorescent substances. G. Y.

Dialkyl Ethers of Chloroaminoresorcinol. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 135331).—When 2 : 4 : 5-trichloro-1-nitrobenzene is acted on by sodium hydroxide in methyl alcohol, it is converted into *chloronitroresorcinol dimethyl ether*, crystallising in pale yellow, iridescent needles melting at 125·5°. If ethyl alcohol be used, the *diethyl ether* is obtained in pale red, silky needles melting at 120·5°. On reduction, these compounds are converted into *chloroaminoresorcinol dimethyl ether*, melting at 90°, and the *diethyl ether*, melting at 63—64°. The *acetyl* derivatives melt at 136—137° and 136° respectively. C. H. D.

Action of Alkaline-earth Bases on the Alkaline-earth Pyrogallolsulphonates. MARCEL DELAGE (*Compt. rend.*, 1903, 136, 893—895. Compare Abstr., 1900, i, 595; 1901, i, 274, 643).—When solutions of the hydroxides of calcium, strontium, or barium are added to aqueous solutions of calcium, strontium, or barium pyrogallolmono- or -di-sulphonates, coloured substances are produced, the composition of which varies with the conditions of the experiment. By carrying out the reaction systematically, six compounds have been obtained, varying in colour from violet to blue. The solubility in water and alcohol increases with increasing molecular weight of the base employed and with the number of sulphonic groups present. They are soluble in acids, giving yellow solutions. In the moist state, they oxidise very easily, and when deposited on silk they turn green, then yellow. When dry, they are fairly stable.

They are most probably formed by the replacement of the hydrogen of the phenolic hydroxyl groups by metal. J. McC.

Diethyl*ortho*hydroxylphenylcarbinol and Derivatives. A. MOUNIÉ (*Bull. Soc. chim.*, 1903, [iii], 29, 350—355. Compare Béhal, Abstr., 1901, i, 246).—*o-Hydroxyphenyldiethylcarbinol*,

$$OH \cdot C_6H_4 \cdot CEt_2 \cdot OH,$$

obtained by the action of ethylmagnesium bromide on methyl salicylate, crystallises from ether, melts at 57°, is soluble in benzene, less so in light petroleum, and insoluble in water; the *methyl ether* similarly obtained from methyl *o*-methoxybenzoate is a colourless liquid which boils at 142° under 18 mm. pressure, has sp. gr. 1·006 at 0°/0° and 0·951 at 15°/15°, and n_D 1·51673 at 17°.

When warmed at 100—110°, the alcohol is converted into o-*ethopropenylphenol*, $OH\cdot C_6H_4\cdot CEt\colon CHMe$, a colourless oil, which boils at 112—113° under 19 mm., at 119—120° under 27 mm., and with decomposition at 215—216° under 753 mm. pressure; it has a sp. gr. 1·012 at 0°/0°, 0·991 at 15°/15°, and n_D 1·53234 at 17°. The *acetate* boils at 132—134° under 23 mm. and at 124—126° under 18 mm. pressure, has a sp. gr. 1·014 at 0°/0° and 1·011 at 15°/15°, and n_D 1·50919 at 17°. The n-*hexoate* boils at 175—177° under 20 mm. pressure, has a sp. gr. 0·980 at 0°/0°, and 0·971 at 15°/15°, and n_D 1·49668 at 17°. The *benzoate* boils at 212—213·5° under 30 mm. pressure, and has a sp. gr. 1·092 at 0°/0° and 1·081 at 15°/15°.

The *methyl ether* boils at 134—136° under 35 mm., at 113—115° under 19 mm. pressure, has a sp. gr. 0·977 at 15°/15°, and n_D 1·52013 at 17°. The *ethyl ether* boils at 121—122·5° under 21 mm. pressure, has a sp. gr. 0·96 at 0°/0° and 0·945 at 15°/15°, and n_D 1·51030 at 17°. The *benzyl ether* is a colourless liquid, which distils at 192—193° under 19 mm. pressure, has a sp. gr. 1·041 at 15°/15°, and n_D 1·55804 at 17°.

The methyl ether, on treatment with bromine, furnishes an unstable *bromide*, which is converted by barium hydroxide into the corresponding *glycol*, a colourless oil with a pinene-like odour; it is volatile in steam, has sp. gr. 1·169 at 0°/0°, 1·126 at 15°/15°, and n_D 1·54631 at 17°.

T. A. H.

Diphenylstyrylcarbinol. ELMER P. KOHLER (*Amer. Chem. J.*, 1903, **29**, 352—363).—*Diphenylstyrylcarbinol*, $CHPh\colon CH\cdot CPh_2\cdot OH$, prepared according to Grignard's reaction by the interaction of benzylideneacetophenone (1 mol.) and phenylmagnesium bromide (2 mols.), crystallises in colourless needles, melts at 96°, is very soluble in acetone, chloroform, benzene, or hot alcohol, and distils under reduced pressure without decomposition. It dissolves in concentrated sulphuric acid with formation of a lemon-yellow solution, from which it is reprecipitated by water.

The *compound*, $C_2H_2(CH_2Ph)_2(CPh_2\cdot OH)_2$, obtained by reducing diphenylstyrylcarbinol with zinc dust and glacial acetic acid, crystallises in small plates, melts at 195°, and is fairly soluble in chloroform or benzene. When diphenylstyrylcarbinol is oxidised with alkaline permanganate, or with a solution of chromic acid in glacial acetic acid, benzoic acid and benzophenone are produced. By the action of bromine on diphenylstyrylcarbinol, a *bromo*-derivative is formed which crystallises in colourless plates, melts at 163°, and is readily soluble in chloroform or ether.

Diphenylstyrylchloromethane, obtained by the action of phosphorus pentachloride on diphenylstyrylcarbinol, crystallises in large, lustrous, monoclinic prisms, melts at 91°, and is readily soluble in glacial acetic acid or hot alcohol.

When benzylideneacetophenone (1 mol.) reacts with phenylmagnesium bromide (1 mol.), a crystalline *substance*,

$$CHPh\colon CBz\cdot CHPh\cdot CH_2\cdot CPh_2\cdot OH$$

or $CHPh\colon CBz\cdot CH(CH_2Ph)\cdot CPh_2\cdot OH$, is produced, which melts at 180° and is readily soluble in acetone, benzene, or hot glacial acetic acid; when heated under 20 mm. pressure, it undergoes decomposition with

formation of benzylideneacetophenone, diphenylstyrylcarbinol, and a yellow oil. It dissolves in concentrated sulphuric acid forming a blood-red solution.

A third product of the action of benzylideneacetophenone on phenylmagnesium bromide is a magnesium compound, which is soluble in ether, and when decomposed with water yields a colourless oil; when this oil is heated under reduced pressure, it undergoes decomposition with formation of stilbene and benzophenone. E. G.

Synthesis of Benzene. Action of Potassium Hydroxide on Dypnone. LOUIS GESCHÉ (*Bull. Acad. Roy. Belg.*, 1903, i, 136—146. Compare Abstr., 1900, i, 603, and 604).—*a-Homodypnopinacolin*, $C_{32}H_{26}O$, produced together with *a-iso*dypnopinacolin by the action of potassium hydroxide in alcohol on dypnone, crystallises in white needles with a silky lustre, melts at 162° when crystallised from benzene, and at 170° when freed from solvents of crystallisation, is soluble in acetone, less so in acetic acid and alcohol, and insoluble in water; it dissolves in sulphuric acid to a slightly orange solution showing green fluorescence.

Homodypnopinacolin is not acted on by acetyl chloride, but is converted by warm, dilute (1·5 per cent.) alcoholic potash into *iso*dypnopinacolin, and by stronger solutions into benzoic acid and a hydrocarbon, $C_{25}H_{22}$. Sodium amalgam reduces it to homodypnopinacolic alcohol. T. A. H.

Action of Silver Cyanate on Aryl Chlorides. OTTO BILLETER (*Arch. Sci. phys. nat.*, 1903, [iv], 15, 335—336).—*Benzoyl cyanate* separates from ether as a white solid which melts at 25·5° and boils at 202·5—204°. When benzenesulphonic chloride reacts with silver cyanate, there are obtained *benzenesulphonyl cyanate* and benzenesulphonic anhydride, $(Ph\cdot SO_2)_2O$, which forms deliquescent, cubical crystals, melts at 92°, and is insoluble in water (compare Abrahall, Trans., 1873, **26**, 606). The cyanates of the acid radicles react with amines, alcohols, amides, and phenols to form carbamides, and in presence of aluminium chloride condense with aromatic hydrocarbons. T. A. H.

So-called Compounds of Salts of Sulphocarboxylic Acids with Sulphuric Esters. ANTOINE P. N. FRANCHIMONT [with ATTEMA] (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, **5**, 482—484).—When a solution containing molecular proportions of the barium salt of ethyl *m*-sulphobenzoate and barium ethyl sulphate is evaporated, needle-shaped crystals of the double salt,

$$(CO_2Et\cdot C_6H_4\cdot SO_3)_2Ba,(EtSO_4)_2Ba,6H_2O,$$

separate; it is decomposed by water and cannot be crystallised from alcohol.

It has not been possible to obtain any double compounds of salts of sulphocarboxylic acids with normal sulphuric esters. J. McC.

Michael's *iso*Cinnamic Acid. CARL LIEBERMANN (*Ber.*, 1903, 36, 1448).—Controversial, in reference to Michael and Garner, this vol., i, 418. T. M. L.

Basic Mercuric Salicylate. HENRI LAJOUX (*J. Pharm. Chim.*, 1903, [vii], 17, 412—418).—Basic mercuric salicylate, $C_6H_4<\genfrac{}{}{0pt}{}{CO_2}{O}>Hg$, dissolves without change in cold or warm alkali hydroxides, being precipitated by acids, including carbonic. It is soluble in alkali chlorides, and is only slowly decomposed by hydrogen sulphide and ammonium sulphide, but is readily decomposed by potassium cyanide. G. D. L.

Preparation of Alkyloxymethyl Esters of Salicylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D R.-P. 137585).—The alkyloxymethyl salicylates, which resemble methyl salicylate in their physiological properties, but are free from odour, may be prepared by the action of halogenmethylalkyl ethers on the salts of salicylic acid.

ω-Methoxymethyl salicylate, $OH\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot OCH_3$, is prepared by adding chlorodimethyl ether, diluted with benzene, to sodium salicylate, suspended in benzene, at a temperature not above 40°. After washing with dilute aqueous sodium carbonate, the solution is dried by means of calcium chloride and fractionally distilled, after evaporating off the benzene. The ester is an almost colourless and odourless oil, boiling at 153° under 32 mm. pressure and evolving formaldehyde when heated at the ordinary pressure. Dilute acids decompose it into salicylic acid, formaldehyde, and methyl alcohol. The *ethyl ester* has similar properties and boils at 168—169° under 43 mm. pressure. C. H. D.

Transformations of Phenyl Carbonate and Phenyl Salicylate. ROBERT FOSSE (*Compt. rend.*, 1903, 136, 1074—1076).—When phenyl carbonate is heated with sodium carbonate at 200—300°, there are formed carbon dioxide, phenol, phenyl ether, *o*-phenoxybenzoic acid, and its phenyl ester, the last predominating when small quantities (5 per cent.) of sodium carbonate are employed, and phenyl *o*-phenoxybenzoate being the principal product when sodium carbonate is in large excess.

It is suggested that the phenyl carbonate is first transformed into phenyl salicylate, since this furnishes the same products when heated with sodium carbonate. T. A. H.

Bromo-derivatives of *p*-Hydroxybenzoic Acid. E. COMANDUCCI and F. MARCELLO (*Gazzetta*, 1903, 33, i, 68—72).—It is stated in text-books that the action of bromine on *p*-hydroxybenzoic acid yields only tribromophenol, but the author finds that, under certain conditions, various bromohydroxybenzoic acids are obtained. Thus, *m*-bromo-*p*-hydroxybenzoic acid is produced by mixing ethereal solutions of molecular proportions of the acid and bromine, or by the absorption of bromine vapour by the acid under a bell-jar; the acid melts at 156° (corr.), and not at 148° as stated by Paal (Abstr., 1896, i, 40).

3 : 5-Dibromo-*p*-hydroxybenzoic acid [$Br_2 : OH : CO_2H = 3 : 5 : 4 : 1$] is formed when the acid (1 mol.) is left for 20 days under a bell-jar in presence of bromine (2 mols.), or when 2 mols. of bromine are added to an acetic acid solution of 1 mol. of the acid. T. H. P.

Synthesis of Indigotin from Thiocarbanilide. TRAUGOTT SANDMEYER (*Zeit. Farb. Text. Chem.*, 1903, **2**, 129—137).—When trichloroethylidenedianilide, $CCl_3{\cdot}CH(NHPh)_2$, is heated with hydroxylamine hydrochloride in alcoholic solution, it apparently gives initially trichloroaldoxime and aniline, which then interact to form iso*nitroso-ethenyldiphenylamidine*, $NPh{:}C(NHPh){\cdot}CH{:}N{\cdot}OH$; the same substance can be prepared directly from chloral hydrate, hydroxylamine, and aniline at 90—110°, and forms a yellow, crystalline powder, which melts at 131—132° and is easily soluble in both acids and alkali hydroxides. When warmed with concentrated sulphuric acid, it gives *a-isatinanilide*,

$$C_6H_4{<}{\substack{-N\\CO}}{>}C{\cdot}NHPh \quad \text{or} \quad C_6H_4{<}{\substack{NH\\CO-}}{>}C{:}NPh,$$

which crystallises from benzene in blackish-violet needles, melts at 126°, and by reduction with ammonium sulphide is converted into indigotin.

As the poor yield of *iso*nitrosoethenyldiphenylamidine in the foregoing synthesis rendered it commercially inapplicable, the following method was devised, having as its starting point hydrocyanocarbodiphenylimide, $NPh{:}C(CN){\cdot}NHPh$ (Laubenheimer and Göring, Abstr., 1881, 163), which appeared to be the intermediate product of the transformation of the *iso*nitroso-compound into a-isatinanilide. This substance is best prepared by warming an aqueous alcoholic solution of thiocarbanilide and potassium cyanide with white lead, but is not directly convertible by sulphuric acid into a-isatinanilide; it is necessary to digest it at 25—35° with a solution of yellow ammonium sulphide, prepared by saturating ammonia with hydrogen sulphide and dissolving sulphur in the product. In this way, *thio-oxamicdiphenylamidine*, $NPh{:}C(NHPh){\cdot}CS{\cdot}NH_2$, is obtained, which crystallises from alcohol in thin, golden-yellow, lustrous prisms, melts at 161—162°, and is easily converted into a-isatinanilide by adding it carefully to concentrated sulphuric acid at 90—95°. The isatinanilide is commercially reduced to indigotin by adding a freshly-prepared solution of ammonium sulphide to its alcoholic solution; the crystalline product so obtained differs from that prepared from isatin chloride or ψ-isatinoxime in containing no indigopurpurin.

When hydrogen sulphide acts on a-isatinanilide in cold acid solution, it gives *a-thioisatin*, $C_6H_4{<}{\substack{-N\\CO}}{>}C{\cdot}SH$ or $C_6H_4{<}{\substack{NH\\CO-}}{>}CS$, as a voluminous, yellowish-brown, unstable precipitate, which is decomposed by aqueous sodium carbonate, yielding indigotin and sulphur; the finely-divided indigotin prepared in this way is better suited for technical purposes than a crystalline product.

[With A. CONZETTI.]—*o*- and *p*-Methylindigotins were obtained in a similar manner, starting with the ditolylthiocarbamides. *Hydrocyanocarbodi*-o-*tolylimide* crystallises from alcohol in well-formed, yellow

prisms, and melts at 107°; the analogous *p*-tolyl *compound* forms bright yellow needles and melts at 124°.

Hydrocyanocarbophenyl-o-*tolylimide*, prepared from phenyl-*o*-tolylthiocarbamide, is a yellow, crystalline powder and melts at 90—91°; the *p*-compound, prepared from phenyl-*p*-tolylthiocarbamide, crystallises from alcohol in slender, yellow needles and melts at 103—104°.

Thio-oxamicdi-o-*tolylamidine* crystallises from alcohol in yellow plates and melts at 139°; the *p*-compound in yellowish-brown plates melting at 143—144°; *thio-oxamicphenyl*-o-*tolylamidine* forms olive-green, lustrous prisms and melts at 134°, and the *p*-tolyl *compound* melts at 139°.

o-*Methylisatin*-α-o-*toluidide*,

$$C_6H_3Me{<}{\begin{smallmatrix}-N\\CO\end{smallmatrix}}{>}C{\cdot}NH{\cdot}C_6H_4Me \text{ or } C_6H_3Me{<}{\begin{smallmatrix}NH\\CO\text{-}\end{smallmatrix}}{>}C{:}N{\cdot}C_6H_4Me,$$

separates from alcohol in small, brownish-red, spear-shaped crystals and melts at 140°; the analogous p-*methylisatin*-α-p-*toluidide* crystallises from benzene in slender, dark brownish-violet needles and melts and decomposes at 180°.

o-*Dimethylindigotin* forms beautiful needles with a coppery lustre, and p-*dimethylindigotin* is a dark blue powder.

Oxamicdiphenylamidine, $NPh{\cdot}C(NHPh){\cdot}CO{\cdot}NH_2$, obtained by the action of hydrogen peroxide on hydrocyanodiphenylimide, forms yellow leaflets, melts at 154—155°, and differs from the analogous thio-compound in failing to give α-isatinanilide with concentrated sulphuric acid. W. A. D.

Synthesis of Homogentisic Acid. WILLIAM A. OSBORNE (*Proc. Physiol. Soc.*, 1903, xiii—xiv; *J. Physiol.*, 29).—The dimethyl ether of homogentisic acid is obtained by adding quinol dimethyl ether, dissolved in excess of carbon bisulphide, to ethyl chloroacetate and aluminium chloride and boiling in a reflux apparatus for 3—5 days. By heating the dimethyl ether with red phosphorus and fuming hydriodic acid, the methyl groups are removed and homogentisic acid is obtained.

W. D. H.

Acyl Derivatives of Phenylglycine-*o*-carboxylic Acid Esters. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 138207).—The acid esters of phenylglycine-*o*-carboxylic acid cannot be acetylated, although other acid groups (compare Abstr., 1902, i, 452) can be introduced into their molecules.

Ethyl hydrogen nitrosophenylglycine-o-*carboxylate*,

$$CO_2Et{\cdot}C_6H_4{\cdot}N(NO){\cdot}CH_2{\cdot}CO_2H,$$

is obtained as a red, viscous oil by the action of sodium nitrite and hydrochloric acid on the ethyl ester. Ethyl chlorocarbonate reacts similarly to form the *urethane* of *ethyl hydrogen phenylglycine*-o-*carboxylate*, $CO_2Et{\cdot}C_6H_4{\cdot}N(CO_2Et){\cdot}CH_2{\cdot}CO_2H$, which is purified by repeated solution in sodium carbonate and precipitation by acid, and then melts at 106—108°. The isomeric *urethane*, $CO_2H{\cdot}C_6H_4{\cdot}N(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$, is similar and melts at 114—116°. C. H. D.

Preparation of Phthalic and Benzoic Acids. BASLER CHEMISCHE FABRIK (D.R.-P. 138790 and 139956).—Naphthols may be oxidised to

n n 2

phthalic acid by fusion with alkali hydroxides above 200° in the presence of a metallic oxide, such as ferric oxide, copper oxide, or manganese dioxide. A portion of the phthalic acid is converted into benzoic acid by loss of carbon dioxide to an extent dependent on the temperature and duration of the process. α-Naphthol produces rather more benzoic acid than β-naphthol. When oxides, for example, ferric oxide, are employed which yield reduction products directly oxidisable by oxygen, less than the calculated quantity of oxide may be added, and air or oxygen forced into the mass. If the process be carried out under pressure at 250—260°, only a slight excess of alkali hydroxide in concentrated solution is necessary, and the proportion of phthalic acid converted into benzoic acid is smaller.

In place of α- or β-naphthol, the product of the fusion of naphthalenesulphonic acids with sodium hydroxide and 1/3 mol. sodium chlorate to oxidise the sulphite to sulphate may be employed directly.

C. H. D.

Phloroglucinolphthalein. CARL LIEBERMANN and TH. ZERNER (*Ber.*, 1903, **36**, 1070—1076).—Phloroglucinolphthalein, prepared from phloroglucinol and phthalic anhydride (compare Link, Abstr., 1881, 95), separates in a hydrated form from water in nearly colourless needles, probably corresponding with the trihydrated lactonic modification, which passes on dehydration into the orange-yellow, quinonoid form. This darkens and sinters at 250°, is easily soluble, forming orange-yellow solutions in alcohol, acetic acid, acetone, and boiling water, sparingly soluble in cold water, and insoluble in benzene and chloroform. Neither these, nor solutions in alkalis or concentrated sulphuric acid, show fluorescence. The compound does not give the phloroglucinol reaction, and is not acted on by alcoholic potassium hydroxide. *Tetrabenzoylphloroglucinolphthalein* and *tetra-acetylphloroglucinolphthalein* both form colourless, amorphous flakes, the latter melting and decomposing at 230°, and dissolve in alcoholic potassium hydroxide displaying a green fluorescence, destroyed by an excess of alkali owing to the complete removal of the acyl groups. But the partially acylated compounds display fluorescence in alcoholic solution on addition of traces of alkali. The *tetrabromo*-derivative forms an amorphous, faintly flesh-coloured substance, dissolving with orange colour in alcohol, and red in alkalis, none of the solutions showing fluorescence. Filter paper containing lime is coloured red by this compound.

On methylation with methyl sulphate, *di-* and *tetra-methylphloroglucinolphthaleins* are produced, and both form yellow substances, the dimethyl ether possessing similar fluorescent properties to those of the partially acylated derivatives. Phloroglucinolphthalein and its derivatives have very feeble tinctorial properties, not colouring the ordinary mordants and yielding feeble tints with the rarer oxides.

Probably the phloroglucinolphthalein derivatives contain the fluoran ring, the absence of fluorescence being due to the presence of two hydroxyl groups in the ortho-positions with respect to the methane carbon atom, as indicated by the development of fluorescent properties, when those groups are acylated or methylated.

G. D. L.

Dihydroxyfluoresceins of Halogen-substituted Phthalic Acids. N. Osorovitz (*Ber.*, 1903, 36, 1076—1084).—*Tetrachlorodihydroxyfluorescein* results from the condensation of tetrachlorophthalic anhydride and hydroxyquinol, and forms green crystals of metallic lustre, very sparingly soluble in organic solvents. Alkali hydroxides, sodium carbonate, and ammonia dissolve the dye to cherry-red, non-fluorescent solutions, whilst the solution in sodium hydrogen carbonate has a rose tint and green fluorescence. After precipitation from alkaline solution, the compound is soluble in alcohol, acetone, and glacial acetic acid, insoluble in benzene and ether. The solution in concentrated sulphuric acid is green and fluorescent, and the dye gives colours with oxide mordants. The *barium* and *calcium* salts form red, crystalline powders. The *hydrochloride* forms red crystals with golden reflex, is soluble in alcohol and ether, and is resolved into its components by water.

The *tetra-acetyl* derivative forms colourless prisms or needles melting at 280°, and is hydrolysed by alcoholic potassium hydroxide. The *dimethyl ether* forms rose-red leaflets with silvery reflex, melts at 275°, gives strongly fluorescent solutions in alkalis and alcohol, and does not form lakes with the ordinary mordants, but gives colours with certain of the rarer oxides. The *trimethyl ether*, $C_{20}H_5O_4Cl_4(OMe)_3$, forms red leaflets with golden reflex, melts at 245°, and resembles the dimethyl compound, differing, however, from it in its insolubility in benzene. On methylation by means of potassium hydroxide and methyl iodide, the carboxyl group is esterified, and a *tetramethyl ether* having the structure $O{<}{\begin{smallmatrix}C_6H_2O(OMe)\\C_6H_2(OMe)_2\end{smallmatrix}}{>}C{\cdot}C_6Cl_4{\cdot}CO_2Me$ is formed as a reddish-yellow powder, melting at 175°, insoluble in cold alkalis, but dissolved on warming, producing solutions of the same appearance as those of the trimethyl ether. The compound is easily soluble in acetone, glacial acetic acid, and alcohol, the latter solution being strongly fluorescent. *Tetrachlorodibromodihydroxyfluorescein*, $C_{20}H_6O_7Cl_4Br_2$, forms dark red leaflets, readily soluble in alcohol and acetone, the former solution being feebly fluorescent, less easily soluble in glacial acetic acid, and forms a bluish-red solution in alkali hydroxides. The basic mordants give intense colours.

Dichlorodihydroxyfluorescein, prepared from 3 : 6-dichlorophthalic anhydride, forms green leaflets, soluble in alcohol, glacial acetic acid, and acetone, the behaviour of which towards alkalis and mordants resembles that of the tetrachloro-compound, like which it forms a barium salt and a hydrochloride. The *tetra-acetyl* derivative forms colourless needles melting at 276°; the *trimethyl ether*, prepared by means of methyl sulphate, separates in violet-red leaflets, which do not colour mordants, and the *dibromo*-derivative forms brown crystals with a golden reflex, which combines with mordants.

Dibromodihydroxyfluorescein, prepared from 4 : 5-dibromophthalic anhydride, forms green crystals soluble in acetone, glacial acetic acid, and alcohol, the latter solution having a green fluorescence, sparingly soluble in water, and insoluble in chloroform and benzene. The alkaline solution is cherry-red, and lakes are formed with mordants.

Dibromodihydroxyfluorescein, on treatment with alcohol and sulphuric acid, gives the *ethyl ester* of the corresponding acid as needles soluble in alcohol, acetone, and glacial acetic acid, slightly soluble in chloroform and ether, and combining with mordants. The alkaline solution is bluer than that of the parent substance, the same tint being produced on keeping. The *triacetyl* derivative of the ester forms yellow crystals melting at 252°. *Tetrabromodihydroxyfluorescein* crystallises from dilute alcohol.

Trihydroxyfluorescein is prepared from 4-hydroxyphthalic acid, and forms dark coloured crystals of metallic lustre, readily soluble in acetone, glacial acetic acid, and alcohol, the latter solution having a strong green fluorescence; the alkaline solution is cherry-red, and lakes are formed with mordants.

A table is given of the absorption bands of the dyes described.

G. D. L.

Preparation of Benzylphthalimides. JOSEPH TSCHERNIAC (D.R.-P. 134979 and 134980).—Hydroxymethylphthalimide reacts with a great variety of aromatic compounds, including hydrocarbons, nitro-compounds, phenols and their ethers, tertiary bases, sulphonic acids, &c., to form benzylphthalimides according to the equation $C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH_2{\cdot}OH + HR = C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH_2R + H_2O$. The benzylphthalimides are decomposed on heating with acids into the corresponding benzylamine bases and phthalic acid.

Strong sulphuric acid is employed as a condensing agent, the concentration and the temperature of reaction being varied according to the compound employed. Thus, benzene is condensed with sulphuric acid of sp. gr. 1·78 with cooling, whilst fuming sulphuric acid at the ordinary temperature, or acid of sp. gr. 1·84 at 50°, is required for nitrobenzene.

o-*Nitrotolylmethylphthalimide*, from *o*-nitrotoluene and hydroxymethylphthalimide, forms small, hard crystals (from alcohol) melting at 155—156°. On adding water to the condensation product, heating to 120°, and separating from phthalic acid, 6-*nitro*-m-*tolylmethylamine*, $NO_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}NH_2$, is obtained as a yellow oil boiling at 169—170° under 12 mm. pressure.

m-*Nitrotolylmethylphthalimide*, from *m*-nitrotoluene, melts at 196—197°; p-*nitrotolylmethylphthalimide* at 175—176°; o-*nitroanisolemethylphthalimide* at 160—161°; and *dimethylaminobenzylphthalimide*, from dimethylaniline, at 104—105°. The latter is hydrolysed by hydrochloric acid to *dimethylaminobenzylamine*, an oil, which could not be distilled. Its hydrochloride, prepared with gaseous hydrogen chloride in ether, crystallises from alcohol in colourless needles melting and decomposing at 212°.

Phenol condenses with hydroxymethylphthalimide to form a mixture of *hydroxyxylylenediphthalimide*, melting at 295°, and two isomeric *hydroxybenzylphthalimides*, crystallising from alcohol and melting at 205° and 150°. *p*-Nitrophenol yields a product, separating from glacial acetic acid and melting at 233—234°, which, on hydrolysis,

forms the base $OH\cdot C_6H_3(NO_2)\cdot CH_2\cdot NH_2$, melting with decomposition at 253° and crystallising from hot dilute ammonia in yellow needles with a golden reflex.

In place of hydroxymethylphthalimide, the compound resulting from the action of concentrated sulphuric acid on this, namely, diphthaliminodimethyl ether (compare Abstr., 1898, i, 475) may be employed. The products are the same as in the former case. C. H. D.

Phthalylhydroxylamic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 135836. Compare Abstr., 1902, i, 720).—Phthalylhydroxylamic acid forms colourless crystals melting and decomposing at 220°. Its solution gives a reddish-brown precipitate with ferric chloride, soluble in excess of the latter to a deep violet solution. The copper salt is grass-green, dissolving in sodium acetate to a dark green solution. Acetic acid forms *phthalylacetylhydroxylamine* melting at 190°. C. H. D.

Esters of Phloroglucinolcarboxylic Acids. JOSEF HERZIG and FRANZ WENZEL [and, in part, KARL EISENSTEIN and BERNHARD BATSCHA]. (*Monatsh.*, 1903, **24**, 101—118. See also Abstr., 1901, i, 473, and 1902, i, 463).—Graetz's methyl methoxyphloroglucinolcarboxylate, $OMe\cdot C_6Me_2(OH)_2\cdot CO_2Me$, when methylated with sodium methoxide and methyl iodide, yields a mixture of products which can be separated by their solubility in potassium hydroxide.

The portion insoluble in potash is *methyl trimethoxydimethylphloroglucinolcarboxylate*, $C_6Me_2(OMe)_3\cdot CO_2Me$, which crystallises from dilute methyl alcohol in white plates melting at 49—50°, and boiling at 178—180° under 15 mm. pressure. It is hydrolysed by alcoholic potash into *trimethoxydimethylphloroglucinolcarboxylic acid*,

$$C_6Me_2(OMe)_3\cdot CO_2H;$$

this melts without decomposition at 125—126°, dissolves in hot water without losing carbon dioxide, crystallises out in needles on cooling, and is characterised by its stability, as it can be heated in a vacuum to 200° before losing carbon dioxide to form *trimethoxydimethylphloroglucinol*, $C_6HMe_2(OMe)_3$. This, when crystallised from methyl alcohol, melts at 61°.

When the portion soluble in potash is saturated with carbon dioxide, *methyl dimethoxydimethylphloroglucinolcarboxylate*,

$$OH\cdot C_6Me_2(OMe)_2\cdot CO_2Me,$$

is precipitated; this crystallises from methyl alcohol in white needles melting at 50—51°, and when hydrolysed with alcoholic potash yields the corresponding *acid*, which melts without decomposing at 125° and does not lose carbon dioxide when heated with water.

When sulphuric acid is added to the filtrate from the preceding ester, *methoxytrimethylphloroglucinol*, $OH\cdot C_6HMe_3O\cdot OMe$, is precipitated as an oil which, when repeatedly boiled with water, goes into solution and crystallises in slender, white needles melting at 179—180° and insoluble in ether; on heating with hydrogen iodide, the methoxy-group is replaced by hydroxyl forming *trimethylphloroglucinol*, $C_9H_{12}O_3$, which melts at 180—181° and dissolves in sodium carbonate with evolution of carbon dioxide.

Similarly, the known tetramethylphloroglucinol melting at 190° has acid properties, as carbon dioxide does not precipitate it from its alkaline solution. Its methyl ether, prepared by alkylation with methyl iodide and potassium hydroxide, is completely hydrolysed by alcoholic potash, whereas the methyl ether of trimethylphloroglucinol cannot be hydrolysed by potash.

Previous experiments having directed attention to the methylation of the nucleus in the case of silver phloroglucinolcarboxylate (Abstr., 1901, i, 473), similar experiments have been made with malonic and resorcylic acids. After prolonged heating of silver malonate with methyl iodide, traces of methyl *iso*succinate were detected, and silver β-resorcylate, when treated in the same manner, yielded traces of a homologue of β-resorcylic acid. E. F. A.

Synthesis of Sinapic Acid. CARL GRAEBE and ERNST MARTZ (*Ber.*, 1903, 36, 1031—1033. Compare this vol., i, 262).—Starting from pyrogallol dimethyl ether [$OH:(OMe)_2 = 1:2:6$], syringaldehyde, $OH\cdot C_6H_2(OMe)_2\cdot CHO$ [$CHO:OH:(OMe)_2 = 1:4:3:5$], has been prepared by treatment with chloroform and sodium hydroxide; the major part of the ether is, however, unacted on, but can be recovered. When heated with sodium acetate and acetic anhydride, the aldehyde is converted into sinapic acid (m. p. 192°). K. J. P. O.

Derivatives of *p*- and *o*-Aminobenzaldehydes. PAUL COHN and LUDWIG SPRINGER (*Monatsh.*, 1903, 24, 87—100).—Gabriel's method (Abstr., 1883, 1105) for the preparation of *p*-aminobenzaldehyde is greatly improved by reducing *p*-nitrobenzaldehyde with sodium hydrogen sulphite, and the crude hydrochloride can be directly acetylated to *p*-acetylaminobenzaldehyde. This crystallises from water in glistening, yellow prisms melting at 161° and forms an oxime melting at 206°, whereas Gabriel found 155° and 206° respectively. The *phenylhydrazone* crystallises from acetic acid in reddish-yellow needles melting at 209°.

3-*Nitro*-4-*acetylaminobenzaldehyde* is formed by nitration in presence of excess of strong sulphuric acid; it crystallises from water in long, yellow needles melting at 155° and forms a *phenylhydrazone* which crystallises in red plates from acetic acid and melts at 209°. On hydrolysis with sodium hydroxide, the known 3-nitro-4-aminobenzaldehyde is formed; this melts at 191°, and its phenylhydrazone forms reddish-brown, glistening plates melting at 202°. Walter and Bretschneider (Abstr., 1898, i, 581) gave 144·5°.

5-*Nitro*-2-*acetylaminobenzaldehyde*, formed by nitration of *o*-acetylaminobenzaldehyde in presence of strong sulphuric acid, crystallises from water in long, white needles melting at 160—161°. The *oxime* crystallises from alcohol in long, white needles and melts at 239°; the *phenylhydrazone* forms yellow needles aggregated in stars from xylene, and melts at 229°. When hydrolysed by boiling with concentrated hydrochloric acid, it yields 5-*nitro*-2-*aminobenzaldehyde*, which crystallises in yellow prisms from alcohol and melts at 200·5—201°; the *oxime* forms long, yellow needles melting at 203°.

When condensed with acetone, 6-*nitro-2-methylquinoline* is formed, which crystallises from water in pale yellow, glistening needles melting at 173—174°. When condensed by heating with acetic anhydride and sodium acetate, the 6-nitrocarbostyril melting at 277°, already described by Friedländer (Abstr., 1885, 1139), is obtained.

E. F. A.

Condensation of *iso*Butaldehyde with *m*-Hydroxybenzaldehyde and *m*-Ethoxybenzaldehyde. WALTHER SUBAK (*Monatsh.*, 1903, 24, 167—173).—Condensation of *m*-hydroxybenzaldehyde and *iso*butaldehyde cannot be effected either in presence of potassium carbonate or alcoholic potash. *m*-Ethoxybenzaldehyde, however, condenses with *iso*butaldehyde in presence of potassium carbonate to form an *aldol*, $C_{13}H_{18}O_3$, probably having the constitution

$$OEt \cdot C_6H_4 \cdot CH(OH) \cdot CMe_2 \cdot CHO,$$

which cannot be distilled. On reduction with sodium amalgam, a *glycol*, $C_{13}H_{20}O_3$, is formed, which boils at 210° under 19 mm. pressure, and when heated with acetic anhydride at 160° yields a *diacetate*, $C_{17}H_{24}O_5$, boiling at 202° under 13 mm. pressure. The same glycol is formed directly on condensing the two aldehydes in presence of alcoholic potash.

E. F. A.

Action of Formaldehyde and Lime on Cinnamaldehyde C. M. VAN MARLE and BERNHARD TOLLENS (*Ber.*, 1903, 36, 1347—1351. Compare this vol., i, 460).—When cinnamaldehyde is left in contact with 40 per cent. formaldehyde solution, water, and lime or baryta at 30—50° for 1—2 days, it is mainly decomposed into benzaldehyde, which can be isolated as such, and acetaldehyde, which can be isolated in the form of penterythritol (Abstr., 1892, 128).

J. J. S.

Formaldehyde Derivatives of Acetophenone. C. M. VAN MARLE and BERNHARD TOLLENS (*Ber.*, 1903, 36, 1351—1357. Compare this vol., i, 460).—Acetophenone and 40 per cent. formaldehyde condense in the presence of ammonium chloride and at the temperature of the boiling water-bath, yielding a mixture of trimethylolbisacetophenone and monomethylolacetophenone, which can be separated by the aid of cold chloroform.

Monomethylolacetophenone (β-hydroxypropiophenone),

$$COPh \cdot CH_2 \cdot CH_2 \cdot OH,$$

is readily soluble in cold chloroform, crystallises from alcohol, melts at 190°, and is decomposed by steam.

Trimethylolbisacetophenone,

$$CH(CH_2 \cdot OH)_2 \cdot CPh{<}^{O}_{O}{>}CPh \cdot CH_2 \cdot CH_2 \cdot OH,$$

is practically insoluble in cold chloroform, melts at 156°, and on oxidation yields benzoic acid. When acetylated, the compound is decomposed and yields the *acetyl* derivative of monomethylolacetophenone, which melts at 54°, together with an anhydro-*compound* melting at 106°.

When distilled in steam, the bis-compound is decomposed, yielding

a volatile oil with a penetrating odour and the non-volatile dimethylolacetophenone. The oil is probably phenyl vinyl ketone, $COPh\cdot CH\colon CH_2$, obtained from the monomethylol. It readily polymerises to a hard, gummy substance, and yields a *dibromide*, $C_9H_8OBr_2$, melting at 53—54°. The same oily compound is formed when monomethylolacetophenone is boiled with water.

Dimethylolacetophenone (*β-benzoylpropan-αγ-diol*),

$$COPh\cdot CH(CH_2\cdot OH)_2 + H_2O,$$

softens at 106°, melts at 116°, and is soluble in alcohol. J. J. S.

Condensation of *p*-Chlorobenzyl Cyanide with Aromatic Esters in Presence of Sodium Ethoxide. REINHOLD VON WALTHER and L. HIRSCHBERG (*J. pr. Chem.*, 1903, [ii], 67, 377—394. Compare Abstr., 1897, i, 524; Erlenmeyer, Abstr., 1900, i, 493; Mehner, Abstr., 1901, i, 208).—p-*Chlorobenzyl cyanide*, formed by the action of *p*-chlorobenzyl chloride on potassium cyanide in aqueous solution, is a clear, refractive liquid which solidifies to thick crystals melting at 30°.

The action of *p*-chlorobenzyl cyanide on ethyl benzoate in presence of sodium ethoxide leads to the formation of p-*chloro-α-cyanodeoxybenzoin*, $C_6H_4Cl\cdot CH(CN)\cdot COPh$, which crystallises from alcohol, melts at 92°, is soluble in glacial acetic acid, benzene, or light petroleum, and dissolves in dilute aqueous sodium hydroxide or ammonia with decomposition into *p*-chlorobenzyl cyanide and benzoic acid. When heated with concentrated hydrochloric acid at 150° under pressure, chlorocyanodeoxybenzoin yields *p*-chlorophenylacetic acid and *p-chlorodeoxybenzoin*, which crystallises in white, glistening leaflets and melts at 133°.

With phenylhydrazine, chlorocyanodeoxybenzoin forms 5-*imino*-1 : 3-*diphenyl*-4-p-*chlorophenylpyrazolone*, $N{\lessdot}\begin{matrix}NPh\cdot C\colon NH \\ CPh-\overset{|}{C}H\cdot C_6H_4Cl\end{matrix}$, which melts at 149°, forms an unstable hydrochloride melting at 210°, and is not decomposed when heated with alcoholic hydrogen chloride under pressure.

With hydroxylamine hydrochloride, chlorocyanodeoxybenzoin forms the *oxime*, $C_6H_4Cl\cdot CH(CN)\cdot CPh\colon N\cdot OH$, which crystallises in needles, melts at 168°, is soluble in aqueous sodium carbonate solution, and insoluble in acids. The action of alcoholic hydrochloric acid on the oxime leads to the formation of 3-*phenyl*-4-p-*chlorophenyl*iso*oxazolone*, which melts at 147°, is easily soluble in ammonia, and insoluble in acids.

With *p*-bromophenylhydrazine, chlorocyanodeoxybenzoin forms a basic substance which melts at 144° and is probably 5-*imino*-3-*phenyl*-1-p-*bromophenyl*-4-p-*chlorophenylpyrazolone*. Withdiphenylhydrazine, the diphenylhydrazone, $C_6H_4Cl\cdot CH(CN)\cdot CPh\colon NPh_2$, is formed; it crystallises in colourless, transparent crystals and melts at 95°.

Chlorodeoxybenzoincarboxylamide, $C_6H_4Cl\cdot CH(COPh)\cdot CO\cdot NH_2$, formed by warming the cyanide with concentrated sulphuric acid, crystallises in slender, white needles, melts at 196°, is soluble in ether, water, and warm aqueous sodium hydroxide and insoluble in acids. It is slowly decomposed by cold dilute sodium hydroxide, with forma-

tion of ammonia, benzoic acid, and chlorophenylacetic acid. The action of hydroxylamine hydrochloride on the amide leads to the formation of the *oxime* of the acid, $C_6H_4Cl\cdot CH(CO_2H)\cdot CPh:N\cdot OH$, which melts at 153°, is soluble in ammonia, only slightly so in aqueous sodium carbonate, and insoluble in acids, and is hydrolysed, with formation of hydroxylamine hydrochloride, when boiled with dilute hydrochloric acid. The *phenylhydrazone*,

$$C_6H_4Cl\cdot CH(CO_2H)\cdot CPh:N\cdot NHPh,$$

formed by the action of phenylhydrazine on the amide, melts at 127°, is soluble in aqueous sodium hydroxide, and insoluble in acids.

Ethyl p-*chlorodeoxybenzoincarboxylate*, $C_6H_4Cl\cdot CH(COPh)\cdot CO_2Et$, formed by the action of hydrogen chloride on the cyanide in absolute alcoholic solution, crystallises in slender needles, melts at 91°, and is hydrolysed by aqueous sodium hydroxide to benzoic and chlorophenylacetic acids. The *methyl* ester melts at 176° and is volatile with steam. The ethyl ester forms a *phenylhydrazone* which melts at 127°.

The action of ammonia on chlorocyanodeoxybenzoin in ethereal solution leads to the formation of an unstable ammonium derivative, but at 160—170° yields *chloroiminocyanodeoxybenzoin*,

$$C_6H_4Cl\cdot CH(CN)\cdot CPh:NH,$$

which crystallises in slender, colourless needles, melts at 174°, and is decomposed by alkalis with evolution of ammonia, by hydrochloric acid with formation of chlorobenzyl cyanide.

Phenylacetyl-p-*chlorobenzyl cyanide*, $C_6H_4Cl\cdot CH(CN)\cdot CO\cdot CH_2Ph$, formed by the action of chlorobenzyl cyanide on ethyl phenylacetate in presence of sodium ethoxide, crystallises in colourless needles, melts at 127°, is soluble in aqueous sodium carbonate solution, insoluble in acids, and is slowly decomposed by aqueous sodium hydroxide to chlorobenzyl cyanide and chlorophenylacetic acid. The *oxime* crystallises in slender prisms and melts at 125°. The *phenylhydrazone* crystallises in slender needles and melts at 131°. *Ethyl phenylacetylchlorophenylacetate*, $C_6H_4Cl\cdot CH(CO_2Et)\cdot CO\cdot CH_2Ph$, crystallises in slender, white needles and melts at 166—168°.

β-Imino-γ-phenyl-α-chlorophenylbutyl cyanide,

$$CH_2Ph\cdot C(NH)\cdot CH(C_6H_4Cl)\cdot CN,$$

formed by the action of ammonia on phenylacetylchlorobenzyl cyanide at 170°, melts at 67—70°. *Hydroxymethylene*-p-*chlorobenzyl cyanide*, $C_6H_4Cl\cdot C(CN):CH\cdot OH$, formed by the action of chlorobenzyl cyanide on ethyl formate in presence of sodium ethoxide, melts at 159—161°, has an acid reaction in aqueous solution, is easily decomposed by sodium hydroxide or ammonia, gives a blue-violet coloration with ferric chloride in dilute solution, and reduces silver nitrate in aqueous solution. G. Y.

Addition of Acids to αβ-Unsaturated Ketones. DANIEL VORLÄNDER and ERICH MUMME (*Ber.*, 1903, 36, 1470—1490).—Acids may react either with the carbonyl oxygen of unsaturated ketones, as supposed by Baeyer and Villiger (Abstr., 1901, i, 658; and 1902, i, 112, 355), or with the double linking. In the former case, the addition of first 1 molecule of acid, followed by 3, as the double bond is also attacked, might be expected, whereas, in the latter case, 2 molecules

of acid only should be added. To settle this, the hydrochlorides of the following ketones have been prepared and analysed. Dibenzylideneacetone, dianisylideneacetone, dianisylidene*cyclo*pentanone, and dicinnamylideneacetone each unite with 2 mols. of hydrogen chloride or 1 of sulphuric acid.

The faintly yellow dibenzylideneacetone becomes orange-red on addition of hydrogen chloride, and the interaction is a momentary one. The hydrochloride is very easily decomposed. The yellow benzylideneacetophenone, on the other hand, unites with hydrogen chloride only slowly, forming a colourless, highly stable salt. These compounds are obtained working either in indifferent solvents or with acetic anhydride, although the latter might be expected to give an acetyl derivative of the coloured form if the enolic constitution attributed to it by Thiele (Abstr., 1899, i, 554) were correct.

The paper closes with a critical discussion of the colour changes due to the formation of additive compounds, and a preliminary stereoelectrical theory is advanced to explain these. E. F. A.

Action of Sulphuric Acid and Acetic Anhydride on Dibenzylideneacetone. Daniel Vorländer and Max Schroedter (*Ber.*, 1903, **36**, 1490—1497).—When dibenzylideneacetone is subjected to the combined action of acetic anhydride and concentrated sulphuric acid, it is oxidised by the acid and acetylated by the anhydride, and so converted into a soluble sulphonic acid, which forms well-crystallised, colourless salts of the composition $C_{17}H_{13}O_2Ac(HSO_3M)$. The *sodium* salt contains $3H_2O$, it decomposes about 240°, and gives no coloration with sulphuric acid. The *potassium* salt is less soluble than the sodium salt; it forms a monohydrate. The *sulphonic acid* forms colourless needles melting and decomposing at 109°; it is easily soluble in water and alcohol, sparingly so in benzene and ether. Alkali hydroxides convert the sodium salt into an *enol*, $C_{17}H_{14}O_2$, which crystallises from alcohol in colourless needles and from acetic acid in prisms sparingly soluble in boiling water; it melts at 176°, gives a brown-violet, ferric chloride reaction, is soluble in alkali, but precipitated from this by carbon dioxide. It forms a *monoacetate*, $C_{19}H_{16}O_3$, melting at 145° and crystallising in colourless plates.

On oxidation, it yields carbon dioxide, oxalic and benzoic acids, but not phthalic acid. Strong alkali hydroxides convert the enol into a *hydrocarbon*, $C_{15}H_{14}$, which crystallises from methyl alcohol in colourless plates melting at 81°, and unites with bromine to form a crystalline *dibromide*, which melts and decomposes at 127°. This is perhaps 7-methylstilbene.

Boiling dilute alkalis convert the enol into deoxybenzoin and acetophenone. The enol is thus probably analogous to the anhydroacetonebenzil compounds described by Japp.

Sulphuric acid monohydrate converts dibenzylacetone into a yellow sulphonic acid. The *sodium* salt, $C_{17}H_{13}O\cdot SO_3Na$, forms colourless needles, dissolves in sulphuric acid with an orange colour, and is decomposed by alkali into benzaldehyde and benzylideneacetone.

E. F. A.

Dibenzylideneacetone Dibromide. PAUL GROEBEL (*Ber*, 1903, 36, 1497—1499).—*Dibenzylideneacetone dibromide*,

$$CHPhBr\cdot CHBr\cdot CO\cdot CH\colon CHPh,$$

obtained by the action of bromine (1 mol.) on the cold chloroform solution of the ketone, crystallises from ether in nearly colourless, prismatic plates, which on heating become yellow at 155°, and melt and decompose at 163°. The solution in concentrated sulphuric acid is coloured yellow. Further action of bromine converts this into the tetrabromide (Claisen and Claparède, Abstr., 1881, 422). Alcoholic potash converts the dibromide into a ketone, which gives a characteristic *hydroxylamine* derivative, $C_{17}H_{13}ON$, forming colourless crystals from alcohol and melting at 126—127°. This is perhaps the *iso*oxazole, $CPh{<}^{CH}_{N\cdot O}{>}CH\cdot CHPh$. E. F. A.

Compounds of Aromatic Aldehydes with *cyclo*Pentanone. CURT MENTZEL (*Ber.*, 1903, 36, 1499—1506).—A series of well-defined compounds of aromatic aldehydes and *cyclo*pentanone are formed by condensation of the components in presence of alkali hydroxides. They all show characteristic colour reactions with concentrated sulphuric acid. *Dicuminylidene*cyclo*pentanone* crystallises from boiling alcohol in long, yellow needles, melting at 143° and dissolving with a red coloration in sulphuric acid. *Disalicylidene*cyclo*pentanone* forms yellow or reddish-yellow plates melting at 190°; the sulphuric acid solution is coloured red. It yields a *dibenzoyl* compound, which forms small, yellow needles from alcohol, melting at 179°.

Di-p-*hydroxydibenzylidene*cyclo*pentanone* forms small, yellow needles which on heating turn brown about 270° and melt above 300°. The sulphuric acid solution is violet-red. The *dibenzoyl* compound forms yellow needles and melts at 229°.

*Divanillylidene*cyclo*pentanone* crystallises with alcohol in yellow prisms which lose the alcohol and become red above 100° and melt at 210°. It gives a blue coloration with sulphuric acid *Dipiperonylidene*cyclo*pentanone* forms dark yellow, prismatic plates melting at 250°, and dissolving in sulphuric acid with a bluish-violet colour. *Di*-m-*nitrodibenzylidene*cyclo*pentanone* melts at 209° and gives an orange-yellow coloration with sulphuric acid. The *tetrabromide* forms colourless, glistening needles, melting and decomposing at 178°; it shows no colour reaction. *Di*-p-*nitrodibenzylidene*cyclo*pentanone* resembles the preceding compound; it melts and decomposes at 240°.

The dinitrodibenzylidene*cyclo*pentanone compounds are easily reduced to the corresponding amino-compounds by stannous chloride, and these form diazo-dyes with naphthylaminesulphonic acids.

*Dibenzylidene*cyclo*pentanone tetrachloride* crystallises in small, white needles from alcohol, or in plates from acetic acid, and melts and decomposes at about 185°. Alcoholic ammonia acts on dibenzylidene-*cyclo*pentanone to form a compound, $C_{31}H_{27}N$, which crystallises from alcohol in yellow prisms melting at 237°. Solutions of this ketone, particularly that in sulphuric acid, are yellow or orange in colour and show a brilliant blue or green fluorescence. It unites with two atoms of

bromine; the microscopic, yellow needles of the additive product become brown at 270°, melt above 300°, and show a similar fluorescence in sulphuric acid.

Nitrous acid forms a nitroso-derivative, $C_{31}H_{26}N{\cdot}NO$, which crystallises with a molecule of acetic acid in small, yellow needles and melts and decomposes at 210—215°. E. F. A.

Preparation of *p*-Chloronitro- and *p*-Bromonitroanthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 137782).—By nitrating α-halogenanthraquinones at a low temperature, *p*-nitro-derivatives are readily and almost exclusively obtained.

1 : 4-*Chloronitroanthraquinone*, 1 : 4-*bromonitroanthraquinone*, 1 : 5-*dichloro*-4 : 8-*dinitroanthaquinone*, 1 : 8-*dichloro*-4 : 5-*dinitroanthraquinone*, and 1 : 5-*dibromo*-4 : 8-*dinitroanthraquinone* are all yellow, crystalline substances dissolving in pyridine, glacial acetic acid, or concentrated sulphuric acid to a yellow solution; when heated with *p*-toluidine, they yield green colouring matters. C. H. D.

Halogen Derivatives of β-Methylanthraquinone. Badische Anilin- & Soda-Fabrik (D.R.-P. 131402).—Halogen derivatives of β-methylanthraquinone are prepared by the action of halogens on mono- or diamino- or mono- or di-alphylaminomethylanthraquinone. The halogen is readily replaced by amine residues.

Bromoamino-β-methylanthraquinone, produced by the action of bromine on amino-β-methylanthraquinone, crystallises from glacial acetic acid in slender, brownish-red needles melting at 215—216° (uncorr.). The corresponding *chloro* derivative, prepared by chlorination in chloroform solution, crystallises from glacial acetic acid in red needles melting at 255—256° (but sintering at 245°).

Tribromodiamino-β-methylanthraquinone, from 1:5-diamino-β-methylanthraquinone, crystallises from nitrobenzene in dark red needles with metallic reflex, and does not melt below 300°. The *trichloro*-derivative also forms red crystals from nitrobenzene, not melting below 300°.

1 : 5-Di-*p*-toluidino-β-methylanthraquinone yields red *chloro*- and *bromo*-derivatives.

On treating a solution of amino-β-methylanthraquinone in chloroform with chlorine as long as the latter is absorbed, a highly chlorinated, yellow product is obtained, in which chlorine appears to be attached to nitrogen. On boiling with a solution of sodium hydrogen sulphite, this is converted into the above-named chloro-derivative.

C. H. D.

Tertiary Bases of the Anthraquinone Series. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 136777 and 136778).—Negatively substituted anthraquinone compounds, containing chloro-, bromo-, nitro-, or hydroxy-groups, readily react with secondary aliphatic amines and with bases of the piperidine type, but not with secondary aromatic amines. The negative radicle is replaced by the amine residue, forming strongly basic compounds, the salts of which, with mineral acids, are undecomposed by water. The condensation takes

place on digesting the compounds together, with or without the addition of alcohol or other solvent, heat being applied in certain cases.

a-Dimethylaminoanthraquinone, from a-nitroanthraquinone and dimethylamine, crystallises from alcohol in long, red prisms, melting at 138°. The salts with mineral acids are colourless, as in the case of all similarly constituted compounds of this series. *a-Piperidino-anthraquinone* forms orange-red leaflets melting at 115°.

1 : 5-*Tetramethyldiaminoanthraquinone*, from 1 mol. of 1 : 5-dinitro-anthraquinone and 2 mols. of dimethylamine, forms brown tablets with green reflex. 1 : 8-*Tetramethyldiaminoanthraquinone*, red crystals (from pyridine). 1 : 8-*Nitrodiethylaminoanthraquinone*, long needles with cantharides lustre, from methyl alcohol. 1 : 8-*Nitropiperidinoanthra-quinone*, dark violet, well-formed crystals from pyridine, melting at 154°. 1 : 5-*Dipiperidinoanthraquinone*, melting at 192°, from methyl alcohol. *a-Piperazineanthraquinone* separates from methyl alcohol in orange-red crystals. *Dimethylaminoanthraquinone-a-sulphonic acid* forms colourless leaflets; its *sodium* salt crystallises from water in glistening, violet needles.

Haloid or hydroxy-derivatives of anthraquinone may similarly be employed. 1 : 4-*Chlorodimethylaminoanthraquinone*, from 1 : 4-dichloro-anthraquinone and dimethylamine, crystallises from alcohol in brownish-red needles melting at 168—170°. 1 : 4-*Dimethylamino-hydroxyanthraquinone*, from dimethylamine and quinizarin, crystallises from pyridine in brownish-red needles with green reflex, melting at 245°; it has both an acid and a basic character, forming a yellow *hydrochloride* and a violet *sodium* salt. 1 : 5-*Piperidinohydroxyanthra-quinone*, from piperidine and anthrarufin, is dark violet and possesses similar properties. 1 : 5-Dichloro-4 : 8-dinitroanthraquinone and di-methylamine yield, according to the temperature of reaction, 1 : 5-*tetramethyldiamino*-4 : 8-*dinitroanthraquinone*, brownish-red crys-tals, or *octomethyltetraminoanthraquinone*, greenish-blue.

p-*Tetramethyldiaminoanthrarufin*, from *p*-dinitroanthrarufin and dimethylamine, is strongly basic. *a-Dimethylaminoalizarin*, from a-nitroalizarin and dimethylamine, separates from aniline in violet-brown crystals. 1 : 5-*Dipiperidino*-4 : 8-*diaminoanthraquinone* forms stable yellow salts with acids.

Derivatives containing more than one negative group may be allowed to react with amines in successive stages, and more than one group thus introduced. 1 : 8-*Dimethylaminopiperidinoanthraquinone* separates from alcohol in brownish-red crystals and melts at 169°.

The process is also extended to negatively substituted arylamino-anthraquinones. Conversely, aniline, &c., may be caused to react with alkylaminoanthraquinones, the same condensation products being obtained in both cases. 1 : 5-p-*Toluidinodimethylaminoanthraquinone* crystallises from alcohol in long, glistening needles. 1 : 5-*Anilino-piperidinoanthraquinone* forms golden, glistening needles ?.

The patent enumerates many analogous compounds. The compounds of this class give characteristic coloured solutions in chloroform, pyridine, glacial acetic acid, and hydrochloric and sul-phuric acids. C. H. D.

Preparation of Nitrogen-free Polychloro-derivatives from Aminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 137074).—When α-aminoanthraquinone and 1 : 3- or 1 : 8-diaminoanthraquinone are dissolved in glacial acetic acid or chloroform and treated with an excess of chlorine, the amino-groups are eliminated, and the product is a mixture of *octochlorodihydroxyanthraquinone* with a small quantity of the *hexachloro*-derivative (compare Abstr., 1902, i, 382). These compounds are yellow powders, dissolving readily in organic solvents with an orange-red colour, and in aqueous sodium hydroxide with an orange or brown colour; with boric and concentrated sulphuric acid, they develop colorations varying from brown to green. C. H. D.

Derivatives of Acenaphthenequinone and their Relations to the Orthodiketones. LUIGI FRANCESCONI and F. PIRAZZOLI (*Gazzetta*, 1903, **33**, i, 36—52).—In its general behaviour, acenaphthenequinone differs considerably from other cyclic diketones and resembles rather the open chain compounds; from both of these types, however, it is distinguished by its reaction with alkalis, the product of which is naphthaldehydic acid. Since, also, under the action of Beckmann's reagent the monoxime of acenaphthenequinone is converted into naphthalimide, this quinone seems to have a tendency to form heterocyclic, six-membered rings.

Acenaphthenequinone monoxime, $C_{10}H_{16}<\begin{matrix}CO\\ |\\ C{:}N{\cdot}OH\end{matrix}$, crystallises from aqueous alcohol in transparent prisms melting at 230°, and is soluble in ethyl acetate, alcohol, acetic acid, or ether; it dissolves in alkalis, and with concentrated sulphuric acid it gives a blue fluorescence which is intensified by keeping or by heating; when boiled with dilute hydrochloric acid, it yields the original ketone. The *acetyl* derivative, $C_{14}H_9O_3N$, separates from alcohol in brown crystals melting at 247° and is soluble in chloroform or ethyl acetate.

Acenaphthenequinone dioxime, $C_{10}H_{16}<\begin{matrix}C{:}N{\cdot}OH\\ |\\ C{:}N{\cdot}OH\end{matrix}$, crystallises from alcohol in white, microscopic prisms, melts at 222°, and dissolves in alkalis giving a yellow coloration, whilst with concentrated sulphuric acid it yields a red coloration and a blue fluorescence; it is not decomposed by hydrochloric acid, but with sulphuric acid it yields acenaphthenequinone. When heated with amyl nitrite, it forms a *peroxide*, $C_{10}H_{16}<\begin{matrix}C{:}N{\cdot}O\\ |\quad\ \ |\\ C{:}N{\cdot}O\end{matrix}$, which is deposited as a lustrous, reddish-brown substance decomposing at about 90° and melting at about 140°; it dissolves slightly in alcohol, more so in ethyl acetate, and readily in chloroform or benzene, and is decomposed by all these solvents into a black substance which remains unmelted at 260°.

Acenaphthenequinone monosemicarbazone, $C_{10}H_{16}<\begin{matrix}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2\\ CO\end{matrix}$, crystallises from dilute alcohol in transparent, microscopic prisms which melt at 192—193° and are very soluble in alcohol or ethyl acetate, and to a less extent in acetic acid, benzene, or water; when

heated with a large proportion of concentrated sulphuric acid, it produces a faint blue fluorescence, whilst with less acid an orange-red coloration is produced. The *disemicarbazone*, $C_{14}H_{12}O_2N_6$, crystallises from dilute alcohol in pale red, microscopic plates or prisms melting at 271°; it is soluble in alcohol, acetic acid, or benzene, and to a less extent in chloroform or ethyl acetate; in alkalis, it dissolves, giving a yellow coloration, and with a large quantity of concentrated sulphuric acid it yields a faint blue fluorescence, whilst with less acid a purple-red coloration is obtained.

Acenaphthenequinone monohydrazone, $C_{10}H_{16}<\begin{matrix}C:N\cdot NH_2\\ | \\ CO\end{matrix}$, separates from acetic acid in slender, yellow prisms which melt at 240—241° and are soluble in alcohol; with sulphuric acid, it gives an intense, blue fluorescence, and on adding more of the substance a characteristic violet coloration is obtained. If the reaction between acenaphthenequinone and hydrazine sulphate is prolonged, the monohydrazone becomes dehydrated, yielding *diazoacenaphthylene*, $C_{10}H_{16}<\begin{matrix}C:N\\ | \quad | \\ C:N\end{matrix}$, which crystallises from dilute alcohol in silky, yellow prisms melting at 164°; it is very soluble in chloroform, ethyl acetate, or acetic acid, and to a less extent in ether, and it gives a characteristic violet coloration with concentrated sulphuric acid.

Acenaphtheneimine, $C_{10}H_{16}<\begin{matrix}CH\\ | \\ CH\end{matrix}>NH$, obtained by reducing the dioxime by means of zinc dust and acetic acid in presence of a few drops of copper chloride solution, forms colourless, microscopic, rhomboidal plates melting at 97°; it dissolves readily in alcohol, benzene, or ethyl acetate, and gives a vivid blue fluorescence with concentrated sulphuric acid. The *hydrochloride* separates from alcohol in microscopic, transparent prisms united in tufts or dendritic aggregates and melting at 280°. The *platinichloride* is deposited in tufts of large, red prisms melting at 230—232°. The *acetate* separates from alcohol in lustrous, microscopic crystals melting at 104°. T. H. P.

Menthyl Glycollate. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 136411).—*Menthyl glycollate* is prepared by heating together glycollic acid and menthol for 6 hours at 175°. The product, which is distilled under reduced pressure and crystallised repeatedly from light petroleum and finally from alcohol, forms white, glistening needles melting at 87°; it is odourless, slightly soluble in water, readily soluble in organic solvents, and is hydrolysed readily by alkalis.

In place of glycollic acid, its silver salt, glycollic anhydride, glycollide, ethyl glycollate, or glycollonitrile may be employed.

C. H. D.

Conversion of Geraniol into *cyclo*Geraniol. HAARMANN & REIMER (D.R.-P. 138141).—Geraniol is decomposed by acids, but if the $-CH_2\cdot OH$ group be protected by esterification, the esters may be converted into derivatives of *cyclo*geraniol by the action of acids.

The products consist of a mixture of α- and β-isomerides in varying proportions, α-*cyclo*geraniol being chiefly formed by the action of phosphoric acid, and the β-compound when sulphuric acid is employed. *cyclo*Geraniol is obtained by hydrolysing the esters with dilute alcoholic soda.

cyclo*Geraniol* boils at 95—100° (corr.) under 12 mm. pressure, and has a sp. gr. 0·935—0·955 at 20°, and the refractive index $n_D = 1·48$; on oxidation with chromic acid, it is converted into *cyclo*citral. cyclo*Geraniol formate* boils at 102—108° under 20 mm. pressure, and has a sp. gr. 0·967 at 18°. The *acetate* boils at 130—132° under 30 mm. pressure, and has a sp. gr. 0·96 at 18°; the *valerate* boils at 145—155° under 20 mm. pressure. These data vary slightly according to the relative proportions of the α- and β-isomerides present. C. H. D.

Preparation of Camphor. AMPÈRE ELECTRICAL CO. (D.R.-P. 134553).—On heating anhydrous pinene with anhydrous oxalic acid at 120—130°, a mixture of camphor, borneol, and the formic and oxalic esters of a terpene alcohol, together with some resinous by-products, is obtained. The camphor may be isolated by fractional distillation. If the mixture be hydrolysed by alkali hydroxides and distilled, dipentene passes over at first, followed by camphor and borneol. The latter may be oxidised to camphor by chromic acid mixture.

In the reaction, pinyl oxalate is first formed as an additive compound, which on heating loses water and carbon monoxide to form camphor, 100 parts being obtained from 350 parts of dry American turpentine, consisting chiefly of *l*-pinene. Some formic acid is produced at the same time, and forms pinyl formate, which then loses carbon monoxide, yielding borneol.

Pinyl formate, $C_{10}H_{17}O{\cdot}COH$, is a colourless, oily liquid boiling and decomposing at 160—163° under 680 mm. pressure; it has a sp. gr. 0·933 at 20°, and does not solidify at −17°.

Pinyl hydrogen oxalate, $C_{10}H_{17}O{\cdot}CO{\cdot}CO_2H$, is solid at the ordinary temperature and boils at 157—160° under 680 mm. pressure; it is decomposed on boiling with water, forming oxalic acid and a mixture of hydrocarbons. C. H. D.

Preparation of a *cyclo*Geraniolanehydroxycarboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 136873).—On treating dihydro*iso*phorone in ethereal solution with sodium and carbon dioxide, *dihydroisophoronecarboxylic acid*,

$$CMe_2<\begin{matrix}CH_2\text{——}CO\\CH_2{\cdot}CHMe\end{matrix}>CH{\cdot}CO_2H,$$

is obtained, melting at 111·5° after crystallisation from benzene. Sodium amalgam reduces it to *hydroxy*cyclo*geraniolanecarboxylic acid*, $CMe_2<\begin{matrix}CH_2{\cdot}CH(OH)\\CH_2\text{—}CHMe\end{matrix}>CH{\cdot}CO_2H$, which separates from ethyl acetate in colourless crystals melting at 180°, and boiling undecomposed at 205° under 10 mm. pressure. The acid is not readily converted into hydroxy*cyclo*geraniolenecarboxylic acid by heating with dehydrating agents. C. H. D.

Alkyl- and Acyl-cyanocamphors and the Esters of Alkylcamphocarboxylic Acids. Influence of the Double Linking of the Nucleus containing the Asymmetric Carbon Atom on the Rotatory Power of the Molecule. ALBIN HALLER (*Compt. rend.*, 1903, 136, 788—792).—In continuation of earlier work on cyanomethylcamphor, which exists both in the ketonic, $C_8H_{14}<\begin{matrix}CR\cdot CN \\ | \\ CO\end{matrix}$, and the enolic, $C_8H_{14}<\begin{matrix}C\cdot CN \\ \| \\ C\cdot OR\end{matrix}$, forms (Abstr., 1891, 1499; and Abstr., 1894, i, 338), other cyanoalkylcamphors have been prepared in order to study the influence on the rotatory power of the double linking present in their enolic forms.

The cyanoalkylcamphors are prepared by adding a solution of sodium methoxide in methyl alcohol to a mixture of cyanocamphor and alkyl iodide, and then fractionally distilling the mixture of ketonic and enolic derivatives which is formed; the latter always boiling at a lower temperature than the isomerides. The ketonic forms are freed from the last traces of the enolic form, which they contain after distillation, by treatment with concentrated hydrochloric acid, when the enolic modification is decomposed into alkyl chloride and cyanocamphor. By this means, the two cyanopropylcamphors have been prepared; the C-*propyl* derivative has $[\alpha]_D + 90°$, and the O-*propyl* derivative $[\alpha]_D + 126°$. C-*Cyanoallylcamphor*, $C_8H_{14}<\begin{matrix}C(CN)\cdot C_3H_5 \\ | \\ CO\end{matrix}$, is an oil boiling at 155—165° under 10 mm. pressure, and has $[\alpha]_D + 49°$; the O-*allyl* compound, $C_8H_{14}<\begin{matrix}C\cdot CN \\ \| \\ C\cdot O\cdot C_3H_5\end{matrix}$, is also an oil boiling at 140—150° under 10 mm. pressure, and has $[\alpha]_D + 124°$; it is readily decomposed by hydrochloric acid. It is noteworthy that the rotatory power of the enolic form is much greater than that of the ketonic form; the same difference is seen in the methyl ($[\alpha]_D + 90°$ and $+ 107°$ respectively) and in the ethyl ($[\alpha]_D + 90°$ and $+ 120°$) derivatives.

Methyl C-propylcamphocarboxylate, $C_8H_{14}<\begin{matrix}CPr^{\alpha}\cdot CO_2Me \\ | \\ CO\end{matrix}$, prepared by adding sodium methoxide to a mixture of methyl camphocarboxylate and propyl iodide (compare Minguin, Abstr., 1891, 1500), is purified by fractionation, when it distils at 165—170° under 10 mm. pressure; it crystallises in prisms melting at 69—70°, has $[\alpha]_D + 52°34'$, and is indifferent towards the ordinary hydrolytic agents. At the same time, a stereoisomeride is formed which melts at 30° and has $[\alpha]_D + 49°44'$.

Methyl *C*-allylcamphocarboxylate has also been prepared by this method, and was found to have properties identical with those ascribed to it by Bruhl (this vol., i, 4). When the ester is heated with 30 per cent. sulphuric acid, it is hydrolysed, and at the same time loses carbon dioxide, yielding *allylcamphor*, $C_8H_4<\begin{matrix}CH\cdot C_3H_5 \\ | \\ CO\end{matrix}$, which is also formed when lead allylhomocamphorate is distilled; it is an oil boiling at 130° under 20 mm. pressure, and gives an *oxime* boiling at

165—170° under 20 mm. pressure; the *semicarbazone* melts at 180°. If the ester is treated with the concentrated instead of dilute sulphuric acid, the lactone, $\begin{matrix} C_8H_{14} \\ | \\ CO \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2\cdot CHMe \\ \quad | \\ CO—O \end{matrix}$, is obtained, forming well-defined crystals melting at 141°; by alcoholic potassium hydroxide, it is converted into the corresponding acid, which forms crystals, but has no definite melting point, as it passes back into the lactone when heated. K. J. P. O.

Ethyl Camphocarboxylate. LOLKE DOKKUM (*Chem. Centr.*, 1903, i, 922—923; from *Pharm. Weekblad.*, 40, 6—7).—*Ethyl camphocarboxylate*, prepared by adding ethyl chlorocarbonate to a solution of camphor in alcoholic sodium hydroxide, is a colourless liquid, soluble in alcohol or ether, but insoluble in water or benzene, and has a sp. gr. 0·915. It has the odour of camphor, but a more bitter taste, and when heated decomposes, forming ethyl carbonate, alcohol, carbon dioxide, and camphor. *Euchinal*, the carboxyethyl esters of the alkaloids of *Cortex Chinæ Succirubræ*, prepared like the preceding compound, is devoid of bitter properties, and may therefore possess a medicinal interest. E. W. W.

Preparation of Camphenilideneacetone. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 138211).—*Camphenilideneacetone*, prepared by the condensation of camphenilanaldehyde with acetone by Claisen's method according to the equation $C_9H_{15}\cdot CHO + CH_3\cdot CO\cdot CH_3 = C_9H_{15}\cdot CH{:}CH\cdot CO\cdot CH_3 + H_2O$, boils at 147—150° under 22 mm. pressure, and has a sp. gr. 0·971 at 15°; it may be employed as a perfume. The *semicarbazone* melts at 178—179°, and the p-*bromophenylhydrazone* at 114—115°. C. H. D.

Derivatives of Ionone. HAARMANN & REIMER (D.R.-P. 133758) (compare Abstr., 1902, i, 471).—On reducing a mixture of α- and β-*cyclo*citrals with sodium amalgam and acetic acid, α-*cyclo*citral remains unaltered, whilst the β-compound is converted into a probably dimolecular derivative having a high boiling point and melting at 129°. The α-semicarbazone melts at 206°.

The homologues of α- and β-ionones are obtained by condensing the corresponding *cyclo*citrals with homologues of acetone in presence of sodium ethoxide:

	Boiling point under 15 mm. pressure (uncorr.).	Sp. gr. at 20°.
α-*Propenylionone* (from α-*cyclo*citral and mesityl oxide) ...	155—165°	0·935—0·940
β-*Propenylionone*	160—172°	0·940—0·945
α-iso*Amyleneionone* (from α-*cyclo*citral and methylheptenone)	165—175°	0·930—0·935
β-iso*Amyleneionone*	170—180°	0·940—0·945
β-*Acetylionone* (from β-*cyclo*citral and acetylacetone) ...	165—175° (20 mm.)	1·00 —1·05

C. H. D.

Reduction in the Terpene Series. FRIEDRICH W. SEMMLER (*Ber.*, 1903, 36, 1033—1040).—In order to avoid isomeric change taking place during reduction of terpene derivatives, the use of sodium and ethyl or amyl alcohol is recommended instead of hydriodic acid. By this means aldehydes and ketones can be reduced to the corresponding alcohols ; at the same time, a double linking is not attacked except when present in a conjugated system containing two such unsaturated linkings.

Many ethereal oils which have an allyl group as a side-chain can be reduced by this means, although a conjugated system of double linkings is not present, but such a system is doubtless formed by rearrangement under the action of the alkali, a change which is not possible in such hydrocarbons as limonene and terpinolene, which cannot be reduced.

Dihydrophellandrene, $C_{10}H_{18}$, is obtained from phellandrene by reduction with sodium and amyl alcohol ; it boils at 171—172°, has a sp. gr. 0·829, and n_D 1·4601 ; on oxidation with permanganate, a very unstable glycol, $C_{10}H_{20}O_2$, is formed, which on further oxidation yields acetic and β-*iso*propylglutaric acids ; the hydrocarbon has accordingly the constitution $CHPr^{\beta}{<}\begin{smallmatrix}CH_2-CH\\CH_2\cdot CH_2\end{smallmatrix}{>}CMe$.

Dihydrolimonene, $C_{10}H_{18}$, cannot be prepared by directly reducing limonene with sodium and alcohol, but the hydrochloride of limonene is converted into a dihydrolimonene when reduced in alcoholic solution at a temperature below 10° ; above this temperature, hydrogen chloride is withdrawn, limonene being reformed. Dihydrolimonene boils at 173—174°, has a sp. gr. 0·829 at 20°, and n_D 1·463. On oxidation, β-*iso*propylglutaric acid is formed. It is yet uncertain whether this hydrocarbon is identical with dihydrophellandrene.

Dihydrotanacetene, $C_{10}H_{18}$, is prepared from tanacetyl alcohol, which is first converted into its chloride and this reduced with sodium and alcohol in the cold. It boils at 164—166° and has a sp. gr. 0·81 at 20° and n_D 1·451.

On reducing carophyllene hydrate, which is formed by the addition of water to the sesquiterpene, carophyllene, with zinc dust under pressure, a hydrocarbon, *dihydro*iso*caryophyllene*, $C_{15}H_{26}$, is produced ; it can also be prepared by converting caryophyllene hydrate into the chloride, $C_{15}H_{25}Cl$, which melts at 64° and boils at 295°, and subsequently reducing the latter with sodium and alcohol ; the hydrocarbon boils at 138° under 19 mm. pressure, and has a sp. gr 0·918 at 20° and n_D 1·4925 ; it is neither oxidised by permanganate nor attacked by bromine. Since caryophyllene hydrate is derived from a hydrocarbon of a constitution different from that of caryophyllene, it is proposed that the name *iso*caryophyllene hydrate be adopted and that the prefix *iso* be used for all derivatives of the same hydrocarbon.

The constitution of the sesquiterpenes is discussed, and the view expressed that they are all referable to a single hydrocymene type.

K. J. P. O.

Bornylene. IWAN KONDAKOFF (*J. pr. Chem.*, 1903, [ii], 67, 280—284).—The xanthate obtained by Tschugaeff's method (Abstr.,

1900, i, 129) from *l*-borneol (m. p. 206—207°, $[\alpha]_D - 37°44'$) melts at 57°, has $[\alpha]_D - 36°77'$, and yields bornylene, which melts at 101—101·5°, boils at 149—149·5°, and has $[\alpha]_D + 10°91'$ (compare Wagner and Bryckner, Abstr., 1900, i, 554). With acetic acid and zinc chloride, this bornylene yields a small amount of the acetate (Abstr., 1902, i, 478), and with hydrogen chloride in light petroleum solution forms a hydrochloride which melts at 123—125°, has $[\alpha]_D + 18°22'$, and on recrystallisation from light petroleum yields two fractions melting at 120—122° and 123—124°. The latter fraction resembles pinene hydrochloride, but contains only 15·82 per cent. of chlorine, and is partly decomposed by water at the ordinary temperature with formation of hydrochloric acid; the residual hydrochloride melts at 125—127° and contains 15·68 per cent. of chlorine. Pinene hydrochloride is not acted on by water in 100 hours at the ordinary temperature. In glacial acetic acid solution, the bornylene forms a hydrochloride which melts at 102—104° and contains 20·45 per cent. of chlorine.

After heating with alcoholic potassium hydroxide at 160° for 10 hours, the bornylene melts at 100—102°, boils at 149—151°, and has $[\alpha]_D + 8°77'$. The author considers that the bornylene formed by Tschugaeff's method is a mixture of bornylene with *iso*bornylene (camphene). G. Y.

Oils of Neroli and of Petit Grain. By Heinrich Wahlbaum and O. Hüthig (*J. pr. Chem.*, 1903, [ii], 67, 315—325. Compare Hesse and Zeitschel, Abstr., 1903, i, 189).—In a specimen of oil of neroli having a sp. gr. 0·8772 at 15° and α_D +3°28', the authors have found *l*-pinene, *l*-camphene, dipentene, decoic aldehyde (see Stephen, Abstr., 1901, i, 160), phenylethyl alcohol, *d*-terpineol, *l*-linalool and its ester, and esters of phenylacetic and benzoic acids. The presence of indole could not be detected, and the oil does not give a pyrrole reaction (Erdmann, Abstr., 1899, i, 621). Contrary to Hesse and Zeitschel's statement (*loc. cit.*), Tiemann and Semmler's fraction boiling at 97—104° under 15 mm. pressure (Abstr., 1894, i, 83) cannot be geranyl acetate, as this boils at 124—125° under 15 mm. pressure.

A specimen of oil of petit grain from Paraguay, having a sp. gr. 0·8912 at 15° and α_D −0°36', contains 47·25 per cent. of esters calculated as linalyl and geranyl acetates. The fraction boiling at 157—166° gives a pyrrole reaction with pine wood and hydrochloric acid, and the furfuraldehyde action with aniline hydrochloride. The portion distilling at 160—170° has a sp. gr. 0·8503, α_D −13°2', and has an odour of pinene, but does not form a nitrosochloride. The fraction distilling at 160—170° gives an odour of *iso*borneol when treated with glacial acetic acid, sulphuric acid, and alcoholic potassium hydroxide. The portion of the oil of higher boiling point contains dipentene having α_D +2°27', linalool, *d*-terpineol, geraniol, geranyl acetate, methyl anthranilate, and a basic substance which has a strong, characteristic odour.

Geranyl acetate, containing 93·4 per cent. of the ester, boils at 109° under 8 mm. pressure and has a sp. gr. 0·9178 at 15° and α_D +1°6'. Linalool is best identified by means of the *phenylurethane* derivative,

formed by the action of phenylcarbimide on the alcohol, which crystallises in needles and melts at 65°. Linalool, obtained from different sources, is found to vary in boiling point from 197° to 200°, in sp. gr. from 0·8687 to 0·8740, α_D from +12°51′ to −14°7′, and in melting point of the phenylurethane from 63—64° to 65—66°. G. Y.

Oil of Roman Camomile. Preparation of Tiglic and Angelic Acids. Edmond E. Blaise (*Bull. Soc. chim.*, 1903, [iii], 29, 327—331).—Angelic, *iso*butyric, and polymethylacrylic acids were obtained by the hydrolysis of oil of camomile, but tiglic acid could not be isolated. Butyl, *iso*amyl, and active hexyl alcohols were also obtained together with anthémol and a neutral, colourless, insoluble substance.

Tiglic acid was prepared from β-hydroxy-α-methylbutyrate, obtained by condensing acetaldehyde with ethyl α-bromopropionate in presence of zinc, by dehydrating it with phosphorus pentachloride and saponifying, with potassium hydroxide in alcohol, the mixture of ethyl esters of tiglic and α-methyl-β-chlorobutyric acids produced when the latter passes into tiglic acid. T. A. H.

Essential Oil of Tuberose Blossoms and its Production during Enfleurage. Albert Hesse (*Ber.*, 1903, 36, 1459—1470).—Distillation of fresh tuberose blossoms gives a distillate with an unpleasant odour, the essential oil being decomposed under these conditions. Extraction with light petroleum gave only 66 grams of essential oil from 1000 kilos. of fresh tuberose blossoms, but after enfleurage the pomade-fat from the same weight of blossoms gave 801 grams of oil, whilst 78 grams were left in the faded blossoms. The tuberose blossoms thus develop during enfleurage 12 times as much oil as was originally present. The chief constituents of the oil are methyl anthranilate, benzyl alcohol (free and as ester), and benzoic esters, whilst the oil from the pomade, unlike that obtained by extraction, contains methyl salicylate. T. M. L.

Getha-Adjak. Maurits Greshoff and Sack (*Chem. Centr.*, 1903, i, 837; from *Pharm. Weekblad.*, 1903, 127).—Getha-Adjak or ardisin resin, the dried juice of *Ardisia fuliginosa*, a Myrsinacea found in Java, is a rusty brown, resinous mass, odourless, tasteless, and insoluble in boiling water. Boiling alcohol dissolves 73 per cent. of the resin, forming a reddish-brown solution, from which, on cooling, an orange-yellow powder separates, whilst a soft orange-red resin remains in solution. The latter may also be extracted from the adjak by boiling absolute alcohol, ether, chloroform, or benzene, and is soluble in 10 per cent. solutions of alkali hydroxides or carbonates, forming bluish-violet solutions, from which it is precipitated by acids. α-Ardisiol, β-ardisiol, and oxyardisiol have been isolated from this resin. *α-Ardisiol*, $C_{35}H_{46}O_{10}$, is an orange substance, which melts at 107°, is soluble in alcohol, ether, or carbon disulphide, forms violet solutions in alkali hydroxides or carbonates, but does not give a coloration with concentrated acids. By sublimation or by the action of alcohol and a small quantity of potassium hydroxide solution, it is converted into β-ardisiol. *β-Ardisiol*, $C_{35}H_{46}O_{10}$, is a pale brown substance which

melts at 183°, is very sparingly soluble in cold, but more readily in hot, water, alcohol, or benzene, and less soluble in chloroform than α-ardisiol. *Oxyardisiol*, $C_{35}H_{46}O_{11}$, is a brownish-yellow substance which melts at 191°, is very sparingly soluble in boiling alcohol, and behaves with acids and alkalis like ardisiol. Ardisiol gives Bornträger's reaction, and is probably therefore an anthraquinone derivative.

E. W. W.

Ononin. II. FRANZ VON HEMMELMAYR (*Monatsh.*, 1903, **24**, 132—154. Compare Abstr., 1902, i, 480).—Crude ononin is obtained in a state of greater purity than previously described by extracting the *Ononis* root with ether-alcohol and precipitating the impurities from the diluted solution with lead acetate; the filtrate freed from lead salts is evaporated in a vacuum and left to crystallise.

Ononetin, prepared from onospin by the action of dilute sulphuric acid, can only be obtained pure when very dilute solutions are employed; it is more conveniently prepared by heating formylononetin with baryta water. On boiling ononetin for a few minutes only with acetic anhydride in presence of sodium acetate, *tetra-acetylononetin* is formed, which crystallises from alcohol in large, colourless prisms melting at 119—120°. When the acetylation is prolonged, a compound, $C_{22}H_{18}O_6$, is the main product; it crystallises from alcohol in large, colourless plates melting at 190°, and is derived from ononetin by addition of two acetyl groups and elimination of a molecule of water. Onospin acetylated in a similar manner gives rise to *hepta-acetylonospin*, $C_{38}H_{40}O_{17}$, without any elimination of water.

Methylformylononetin, prepared from formylononetin by the action of sodium methoxide and methyl iodide in sealed tubes at 140°, crystallises in broad, colourless plates melting at 156°. The methoxy-determination by Zeisel's method yields results in agreement with the theoretical value for 2 methoxy-groups, whereas both formylononetin and ononetin always give values much too low, presumably on account of a partial carbonisation. Methylformylononetin loses formic acid when heated with aqueous potassium hydroxide, forming methylononetin, $C_{19}H_{18}O_5$; this melts at 95—100° and is sparingly soluble in cold alkali hydroxides.

When fused with potassium hydroxide, formylononetin yields, among other products, 2 : 4-dihydroxybenzoic acid (β-resorcylic acid), as well as some unchanged ononetin. It thus contains two hydroxy-groups in the meta-position, and probably a side-chain linked to one of the neighbouring carbon atoms. E. F. A.

Trimethylbrazilone. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1903, **36**, 1220—1222. Compare Abstr., 1902, i, 483; Gilbody and Perkin, Proc., 1899, **15**, 27, 75; 1900, **16**, 105; Kostanecki and Lampe, Abstr., 1902, i, 481; Kostanecki, this vol., i, 193; Perkin, Trans., 1902, **81**, 1048).—The difference in melting point observed by the authors and Perkin in the different specimens of trimethylbrazilone is accounted for by the fact that the compound exists in two modifications, the one melting at 160—162° and the other at 181—185°. The substance with the higher melting point is trans-

formed into the more fusible isomeride when recrystallised from alcohol or acetic acid. When the compound melting at 160—162° is rubbed with a fragment of the compound of higher melting point, its melting point is immediately raised to 179—180°. No chemical difference in the two compounds has been detected. J. J. S.

Trihydromethylenefurfuranoxime and its Compound with Hydrogen Chloride. KURT SCHEDA (*Ber.*, 1903, 36, 1379—1383).—Lipp's α-methylenetetrahydrofurfuran (Abstr., 1890, 20) is shown to be identical with W. H. Perkin's acetyltrimethylene (Abstr., 1884, 1155; and Trans., 1885, **47**, 834; 1891, **59**, 865). Both are colourless oils distilling at 112—113°, and both yield an oxime melting at 50°. An oily isomeride is formed at the same time, and yields an additive compound with hydrogen chloride which melts at 90°; on treatment with sodium carbonate solution, this is transformed into the crystalline oxime melting at 50°. The solid oxime reacts with an ethereal solution of hydrogen chloride, yielding a product which melts at 140°; this is not a simple additive compound. J. J. S.

4-Amino-1-benzoyl-2-methylcoumarone and its Derivatives. FRANZ KUNCKELL and W. KESSELER (*Ber.*, 1903, 36, 1260—1262).—4-*Acetylamino-1-benzoyl-2-methylcoumarone*,

$$NHAc\cdot C_6H_3<\overset{-O-}{\underset{CMe}{}}>C\cdot COPh,$$

prepared from 5-acetylamino-2-hydroxyacetophenone and ω-bromoacetophenone, crystallises from alcohol in yellow needles and melts at 178—179°. The *oxime*, $NHAc\cdot C_6H_3<\overset{-O-}{\underset{CMe}{}}>C\cdot CPh\colon NOH$, melts at 192°.

4-*Amino-1-benzoyl-2-methylcoumarone*, prepared by hydrolysing the acetyl derivative, crystallises from alcohol in golden-yellow flakes and melts at 138°; the *hydrochloride* separates from alcohol in small, white needles and melts at 245°.

The 4-*acetylamino-1-p-dimethylbenzoyl-2-methylcoumarone*,

$$NHAc\cdot C_6H_3<\overset{-O-}{\underset{CMe}{}}>C\cdot CO\cdot C_6H_3Me_2,$$

prepared by condensing with p-xylyl chloromethyl ketone, crystallises from alcohol in small, white needles and melts with decomposition at 200—205°. T. M. L.

Preparation of Alkyl and Aryl Derivatives of Chloroaminofluoran. FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 139727).—When fluorescein chloride or dichlorofluorescein chloride is heated with the hydrochlorides of fatty or aromatic amines in presence of zinc chloride to 160—170°, derivatives of chloroaminofluoran are formed. At a higher temperature, rhodamines are produced. Sufficient zinc oxide is added to the mass to fix the chlorine set free.

Chlorodiethylaminofluoran, from diethylamine hydrochloride and fluorescein chloride, separates from alcohol in red crystals melting at 148°; it is insoluble in water, sparingly soluble in hot strong hydrochloric acid to a reddish-yellow solution. The alcoholic solution is colourless, becoming red on addition of acids. *Trichlorodiethylamino-*

fluoran, from dichlorofluorescein chloride, is a pale pink powder. *Chloro-methyl-* and *dimethyl-aminofluoran* form pink crystals (from alcohol) and melt at 168° and 218° respectively. C. H. D.

A Reaction in which Symmetrical Diarylpyrones [Xanthones] are produced. ROBERT FOSSE (*Compt. rend.*, 1903, 136, 1006—1009).—When orthophosphoric esters of phenols are warmed with potassium carbonate, diaryl pyrones (xanthones) are formed. From triphenyl orthophosphate, diphenopyrone (xanthone), $C_4H_6<^{CO}_{O}>C_6H_4$, is formed. 4 : 5-*Dimethylxanthone* is obtained from tri-*o*-tolyl orthophosphate. From tri-α-naphthyl orthophosphate, *di*-α-naphthaxanthone is obtained.

J. McC.

General Reaction of Condensation between β-Naphthol, Aldehydes, and Amines. IV. Structure of the Compounds obtained with Ammonia. MARIO BETTI (*Gazzetta*, 1903, 33, i, 17—26. Compare Abstr., 1901, i, 81, 611, and 753).—The condensation taking place between β-naphthol, an aldehyde, and an amine gives rise to a naphthoxazine compound of the formula $C_8H_6<^{C\cdot CHR\cdot NH}_{C\cdot O——CHR}$. When ammonia is employed in place of the amine, the condensation yields, in addition to a naphthoxazine derivative, a compound having an open side-chain: $C_8H_6<^{C\cdot CHR\cdot N:CHR}_{C\cdot OH}$. The latter compounds give, with ferric chloride in the cold, intense red or violet colorations similar to those obtained with many derivatives containing free naphtholic hydroxyl, whilst the naphthoxazines, even when heated, give but a transitory coloration; further, they yield acetyl and benzoyl derivatives which give no coloration with ferric chloride, and on hydrolysis readily lose 1 molecule of the aldehyde forming the corresponding β-naphtholaldamine.

From the condensation product of β-naphthol, benzoylvaleraldehyde, and ammonia, the following three compounds were obtained: (1) 2-*phenyl*-4-*butyl*-1 : 3-β-*naphth*iso*oxazine*,

$$C_8H_6<^{C\cdot CH(C_4H_9)\cdot NH}_{C\cdot O————CHPh},$$

which crystallises from alcohol in mammillary aggregates of silky, white needles melting at 128°. (2) 4-*Phenyl*-2-*butyl*-1 : 3-β-*naphth*iso*oxazine*, $C_8H_6<^{C\cdot CHPh\cdot NH}_{C\cdot O——CH\cdot C_4H_9}$, separating from alcohol in white needles melting at 137°. Both these compounds remain undecomposed when boiled with dilute hydrochloric acid, and they only give a temporary coloration when heated with ferric chloride. (3) β-*Naphtholamylbenzylideneamine*, $C_8H_6<^{C\cdot CH(C_4H_9)\cdot N:CHPh}_{C\cdot OH}$, which crystallises from alcohol in yellow needles melting at 154°; it is readily decomposed by boiling with dilute hydrochloric acid, yielding benzaldehyde and β-naphtholamylamino hydrochloride its benzene

solution gives an intense reddish-violet coloration with ferric chloride in the cold.

The condensation product of β-naphthol, benzaldehyde, and ammonia forms a *benzoyl* derivative, $C_{31}H_{23}O_2N$, which crystallises from alcohol in white needles melting at 224—225°.

The interaction of ethyl iodide and β-naphtholbenzylidenebenzylamine yields different products according to the conditions employed, in one case, β-naphtholbenzylamine hydriodide being formed, and in another, benzylidenedinaphthyl oxide. T. H. P.

β-Naphthoxazines and Allied Compounds containing Mixed Aldehydic and Ketonic Radicles. Mario Betti [with Virgilio Foà] (*Gazzetta*, 1903, 33, i, 27—35).—Both aliphatic and aromatic aldehydes condense readily with β-naphtholbenzylamine, the former yielding naphthoxazine derivatives and the latter hydroxy-compounds having an open side-chain (see preceding abstract), as also do furfuraldehyde and aliphatic ketones. All attempts to prepare naphthoxazine derivatives from aromatic aldehydes have been unsuccessful.

The action of formaldehyde on β-naphtholbenzylamine yields (1) a small quantity of a substance melting at about 210°, and (2) a *compound*, $C_{20}H_{19}O_2N$, which crystallises from a mixture of light petroleum and benzene in rectangular plates melting at 103°; it is soluble in ether, ethyl acetate, or acetone, and on heating with ferric chloride, its benzene solution gives a reddish-violet coloration, which disappears on cooling. When its solution in alcohol, benzene, ethyl acetate, &c., is boiled, it is transformed into *β-naphthoxazinebenzylidenemethyleneamine* (*4-phenyl*-1 : 3-*β-naphth*iso*oxazine*), $C_8H_6<\begin{matrix}C\cdot CHPh\cdot NH \\ \| \qquad\qquad | \\ C\cdot O \text{———} CH_2\end{matrix}$, which crystallises from ethyl acetate as a powder melting at 214°, and is soluble in benzene; it is not changed by boiling with dilute hydrochloric acid. Its 2-*acetyl* derivative separates from light petroleum as a faintly yellow, crystalline powder melting at 142°.

Furfuraldehyde and β-naphtholbenzylamine yield *β-naphtholbenzylfurylideneamine*, $OH\cdot C_{10}H_6\cdot CHPh\cdot N\colon CH\cdot C_4H_3O$, which crystallises from alcohol in brownish-yellow aggregates melting at 115—116°; its benzene solution gives an intense, violet coloration with ferric chloride in the cold, and when boiled with dilute hydrochloric acid it yields furfuraldehyde and β-naphtholbenzylamine hydrochloride.

Salicylaldehyde and β-naphtholbenzylamine react together, yielding *β-naphtholbenzylsalicylideneamine*, $OH\cdot C_{10}H_6\cdot CHPh\cdot N\colon CH\cdot C_6H_4\cdot OH$, which is deposited from alcohol in minute, yellow crystals melting at 174°; when boiled with dilute hydrochloric acid, it gives salicylaldehyde and β-naphtholbenzylamine hydrochloride, and its benzene solution forms a violet coloration with ferric chloride in the cold.

β-Naphtholbenzylcinnamylideneamine,

$$OH\cdot C_{10}H_6\cdot CHPh\cdot N\colon CH\cdot CH\colon CHPh,$$

prepared from cinnamaldehyde and β-naphtholbenzylamine, melts at 174° and is soluble in benzene, alcohol, or ethyl acetate; with hydrochloric acid, it yields cinnamaldehyde, and its benzene solution gives a reddish-brown coloration with ferric chloride in the cold.

*β-Naphtholbenzyl*iso*propylideneamine*, $OH\cdot C_{10}H_6\cdot CHPh\cdot N:CMe_2$, obtained by the interaction of acetone and β-naphtholbenzylamine, melts at 124° and is soluble in alcohol or benzene; in the latter, it yields an intense, violet coloration with ferric chloride in the cold; when boiled with 20 per cent. potassium hydroxide solution, it gives off acetone and ammonia.

*Ethyl β-naphtholbenzylamine*iso*propylidenecarboxylate*,

$$OH\cdot C_{10}H_6\cdot CHPh\cdot N:CMe\cdot CH_2\cdot CO_2Et,$$

prepared from ethyl acetoacetate and β-naphtholbenzylamine, separates from alcohol in white needles melting at 165°; it is decomposed by boiling with either dilute hydrochloric acid or 20 per cent. potassium hydroxide solution, and its benzene solution gives an intense, violet coloration with ferric chloride in the cold. T. H. P.

Alkaloids of Adlumia Cirrhosa. JULIUS O. SCHLOTTERBECK and H. C. WATKINS (*Pharm. Arch.*, 1903, 6, 17—22. Compare Abstr., 1900, ii, 746).—In the investigation of *Adlumia cirrhosa*, described in this paper, the entire plant was employed. Protopine, β-homochelidonine, adlumine, adlumidine, and another *alkaloid* which is present in small quantity and melts at 176—177°, were isolated, together with tartaric and citric acids. The colour reactions of each alkaloid are described.

Adlumine, $OH\cdot C_{37}H_{34}O_9N(OMe)_2$, melts at 188°, forms large, colourless, orthorhombic crystals, and has $[\alpha]_D + 39\cdot 88°$; its *aurichloride* was prepared.

Adlumidine, $C_{30}H_{29}O_9N$, crystallises in small, square plates and melts at 234°. E. G.

Preparation of Atropinium Alkyl Nitrates. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 137622 and 138443).—The atropinium alkyl nitrates may be prepared by the action of the nitrates of the heavy metals upon atropinium alkyl haloids or sulphates, by the action of nitric acid on the free bases, or by heating an alcoholic solution of atropine with alkyl nitrates under pressure.

Atropinium methyl nitrate forms white crystals, dissolving readily in water and alcohol, but sparingly soluble in ether, acetone, and chloroform; it melts at 163° after drying at 100°. *Atropinium ethyl nitrate* is similar, and melts at 116—118°. These compounds possess the therapeutic qualities of atropine without its dangerous effects.

C. H. D.

Acyl Derivatives of Aminocaffeine. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 139960).—Aminocaffeine readily forms acyl derivatives, which strongly resemble theobromine in their diuretic properties. *Acetylaminocaffeine*, from aminocaffeine and acetic anhydride in glacial acetic acid, melts at 270° and dissolves in hot water, alcohol, or cold dilute alkali hydroxides. When excess of acetic anhydride is employed, the product is *diacetylaminocaffeine*, crystallising from alcohol and melting at 145°. The *propionyl*, *dipropionyl*, and *chloroacetyl* derivatives melt at 220°, 140°, and 208° respectively, and closely resemble the acetyl derivative. C. H. D.

Salicylyl Derivatives of the Cinchona Alkaloids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 137207).—When the cinchona alkaloids are dissolved in chloroform and heated with salicylide or polysalicylide in an autoclave at 150°, the salicylic esters are formed.

Salicylyl chloride reacts similarly at a lower temperature. The solution is shaken with acetic acid to remove any free alkaloid, and then with dilute mineral acid to extract the ester, which is then precipitated by means of alkali carbonate, and dissolved in ether. Salicylquinine melts at 140° (Abstr., 1902, i, 486). *Salicylcinchonidine* is a white, sandy powder melting at 65—70°. C. H. D.

Preparation of Acetylquinine. Chemische Fabrik von Heyden, Aktien-Gesellschaft (D.R.-P. 134370).—Hesse's acetylquinine (compare Abstr., 1880, 615), melting at 108°, has an intensely bitter taste. This is due to partial hydrolysis, caused by the use of water or alcohol during the preparation. If the preparation is carried out in the absence of these solvents, or if the crude product is recrystallised from light petroleum or some other solvent free from alcohol and water, acetylquinine is obtained in colourless crystals, melting at 116—117°, without taste at first, but becoming slightly bitter on the tongue owing to partial hydrolysis. C. H. D.

Symmetrical Carbonic Esters of the Cinchona Alkaloids. Vereinigte Chininfabriken Zimmer & Co. (D.R.-P. 134307 and 134308).—By the action of aryl carbonates on cinchona alkaloids, mixed carbonates have been prepared (compare Abstr., 1901, i, 738). If 2 mols. of the alkaloid be caused to react with 1 mol. of the aryl carbonate at 120—130° or at higher temperatures, the product is the symmetrical ester. Thus, dry quinine and phenyl carbonate yield *diquinine carbonate*, $CO(C_{20}H_{23}O_2N_2)_2$, melting at 185·5°. In place of phenyl carbonate, the carbonates derived from guaiacol or thymol may be employed. C. H. D.

Action of Bromine on the Isomeric Cinchonine Bases. R. Zwerger (*Monatsh.*, 1903, 24, 119—131).—When brominated in carbon tetrachloride solution, α-*iso*cinchonine yields a yellow substance, α-iso*cinchonine perbromide*, $C_{19}H_{22}ON_2Br_2$; in other solvents, where secondary action with the solvent is possible, cinchonine hydrobromide is always the only product of bromination. Similarly, β-iso*cinchonine perbromide* and orange-yellow prisms of allo*cinchonine perbromide* are formed from the respective alkaloids in carbon tetrachloride solution, whereas from a mixture of chloroform and alcohol, *trihydrobromocinchonine* is obtained in colourless prisms melting at 242—243°.

The index of refraction of molecular solutions of the acid hydrochlorides of the four isomeric cinchonine bases is found to be practically the same (n_D 1·3777—1·3785). E. F. A.

Piperylhydrazine. Felix B. Ahrens and Sollmann (*Chem. Centr.*, 1903, i, 1034; from *Chem. Zeit.*, 2, 414. Compare Abstr., 1898, i, 686).—By the electrolytic reduction of solutions of nitroso-3-methyl-

piperidine and nitroso-4-methylpiperidine in 50—60 per cent. solutions of sulphuric acid, 3-pipecolylhydrazine and 4-pipecolylhydrazine have been obtained respectively; the latter boils at 160—165°. Under similar conditions, nitroso-2 : 6-dimethylpiperidine yields 2 : 6-dimethylpiperylhydrazine, boiling at 170—175°, and nitrosoaldehydocopellidine and nitroso-*s*-trimethylpiperidine form the corresponding hydrazines, which boil at 180—185°. All the above hydrazines emit strong and stupefying odours, and form dense fumes with hydrogen chloride.

E. W. W.

Constitution of α-Pyridone. HUGO KAUFFMANN (*Ber.*, 1903, **36**, 1062—1063).—In order to decide whether α-pyridone is represented by the formula $CH{<}{}^{CH\cdot CO}_{CH:CH}{>}NMe$, or, as Fischer (Abstr., 1898, i, 382; 1899, i, 633, 635) maintains, by the formula $\begin{matrix} CH\cdot CH:C\text{---} \\ \| \qquad\quad | \\ CH\cdot CH:NMe \end{matrix}{>}O$, in which the nitrogen is quinquevalent, the behaviour of its vapour under the influence of the Tesla-current has been investigated. The vapour became luminescent, with a blue colour, and behaves, therefore, in the same manner as pyridine and its alkyl derivatives. Pyridone is therefore represented by the second formula.

K. J. P. O.

Researches in the Pyridine Series. III. WILLY MARCKWALD and K. RUDZIK (*Ber.*, 1903, **36**, 1111—1120).—Marckwald has shown (Abstr., 1899, i, 72) that α- and γ-chloropyridines interact with hydrazine hydrate to form pyridylhydrazines. It has further been noted by Marckwald and Meyer (Abstr., 1900, i, 519) that triazole and tetrazole derivatives may be obtained from α-quinolylhydrazine, where the latter acts in its tautomeric form.

6-Hydrazinonicotinic acid behaves in an analogous fashion in the tautomeric form $NH_2\cdot N:C{<}{}^{CH:CH}_{NH\cdot CH}{\geqslant}C\cdot CO_2H$.

When 6-chloronicotinic acid is heated at 120—125° with 50 per cent. aqueous solution of hydrazine hydrate, the main product is the *hydrazide*, $NH_2\cdot NH\cdot C{\leqslant}{}^{CH:CH}_{N-CH}{\geqslant}C\cdot CO\cdot NH\cdot NH_2$, melting at 217—218°. It forms white crystals containing $1H_2O$, is a strong reducing agent, and is a di-acid base. Its *picrate* melts and decomposes at 192—193°. It forms a yellow, crystalline *dibenzylidenehydrazone* melting at about 313°; the *dicinnamylidenehydrazone* melts at 265°. With phenylthiocarbimide, it yields a yellow *dithiosemicarbazide* melting at 170—171°.

6-*Hydrazinonicotinic acid*, $NH_2\cdot NH\cdot C{\leqslant}{}^{CH:CH}_{N-CH}{\geqslant}C\cdot CO_2H$, obtained from the mother liquor from which the hydrazide had been crystallised, forms white crystals melting at 283°. It reduces ammoniacal silver solution and forms salts with bases and acids. Its *sulphate* is sparingly soluble in water.

The acid can also be easily prepared by boiling its hydrazide with

aqueous hydrogen chloride. Hydroxynicotinic acid is formed when the hydrazide, or the acid itself, is heated at 150° with hydrogen chloride. The hydrazinonicotinic acid forms, with benzaldehyde, a *benzylidene-hydrazone,* which melts and decomposes at 281°; the *cinnamylidenehydrazone* melts at 263—264°. By the action of potassium cyanate on its hydrochloride, *pyridylsemicarbazidecarboxylic acid,*

$$NH_2\cdot CO\cdot NH\cdot NH\cdot C_5NH_3\cdot CO_2H,$$

is obtained. It forms white crystals melting at 277—278°, and reduces ammoniacal silver solution.

Phenotriazolecarboxylic acid, $\begin{array}{l} CH{:}CH\cdot C{=}N \\ CO_2H\cdot C{=}CH\cdot N\cdot CH \end{array}\!\!>\!N$, prepared by heating 6-hydrazinonicotinic acid with formic acid, forms white crystals and gives salts with bases but not with acids. When oxidised by alkaline permanganate, it is converted into triazole.

Phenotetrazolecarboxylic acid, $\begin{array}{l} CH{:}CH\cdot C{:}N \\ CO_2H\cdot C{=}CH\cdot N\cdot N \end{array}\!\!>\!N$, prepared from the hydrochloride of 6-hydrazinonicotinic acid and potassium nitrite, crystallises in slender, white needles. It can be oxidised to tetrazole. Its *azide* forms beautiful crystals melting at 103—104°; it is comparatively stable, and can be crystallised from hot alcohol.

The *hydrochloride, sulphate,* and *picrate* of 2 : 6-*dimethylpyridyl-4-hydrazine,* $NH_2\cdot NH\cdot C\!<\!\begin{array}{l} CH{:}CMe \\ CH\cdot CMe \end{array}\!\!>\!N$, are described. With benzaldehyde, the base forms a *benzylidenehydrazone,* which melts and decomposes at 220—224°. The *semicarbazide* melts and decomposes at 268—269°. The *phenylthiosemicarbazide* separates in white crystals melting at 199°.

2 : 6-*Dimethylpyridyl-4-phenylhydrazine,* $NHPh\cdot NH\cdot C_7H_8N$, prepared from 4-chloro-2 : 6-lutidine and phenylhydrazine, forms white crystals, and melts indefinitely at 172—180°; its *hydrochloride* melts at 262°, and is remarkably stable towards reducing agents; when boiled with hydriodic acid and red phosphorus for three hours, the base can be reduced to aniline and aminolutidine. Its constitution was further proved by its conversion into its *azo*-derivative, $PhN{:}N\cdot C_7H_8N$, which separates from light petroleum in deep red crystals melting at 62—63°, and can be reconverted into the hydrazo-compound by reducing agents. The *platinichloride, picrate,* and *dichromate* of the azo-compound are described. A. McK.

Lutidines from Coal Tar. FELIX B. AHRENS and GORKOW (*Chem. Centr.,* 1903, i, 1034; from *Chem. Zeitschr.,* 2, 414).—3 : 5-Dimethylpyridine and 2 : 5-dimethylpyridine have been isolated from English coal tar. The latter melts at 159—160° (corr.), and forms the following crystalline salts: $C_7H_9N,HCl,6HgCl_2$; $C_7H_9N,HAuCl_4$; $(C_7H_9N)_2,H_2PtCl_6,2H_2O$; $C_7H_9N,C_6H_2(NO_2)_3\cdot OH$.

2 : 5-Dimethylpiperidine, prepared by reducing 2 : 5-dimethylpyridine, boils at 138—140°; the following salts were prepared: $C_7H_{15}N,HCl$ $C_7H_{15}N,HBr$; $C_7H_{15}N,HI$; $(C_7H_{15}N)_2,H_2PtCl_6$; $C_7H_{15}N,HAuCl_4$.

E. W. W.

[Methylated Indoles and their Sulphonic Acids.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 137117).—The methylindolesulphonic acids previously described have the sulpho-group in the pyrrole ring (compare Abstr., 1895, i, 145). By the use of fuming sulphuric acid below 60°, sulphonation in the benzene ring may be carried out. The acids condense with ketones of the type of *p*-diaminobenzophenone and auramines to form colouring matters. They also combine with diazo-compounds, even in presence of a large excess of acid.

The acids are separated by means of their soluble crystalline barium salts.

The preparation of 2 : 5 : 4-*dimethyl*-1-*ethylindole* (colourless crystals melting at 470°) from acetone and *as*-*p*-tolylethylhydrazine, and of 1 : 2 : 5-*trimethylindole* (colourless leaflets melting at 56—57°) from methyl-*p*-tolylhydrazine, is also described. C. H. D.

Ammonium Compounds. Action of Alkalis on Quinoline-methiodides. Herman Decker (*Ber.*, 1903, 361, 205—1215).—Further analyses of 3-bromo-5-nitro-2-hydroxy-1-methyl-1 : 2-dihydroquinoline (Abstr., 1892, 880) prove that it is not an anhydrodimolecular compound (La Coste, Abstr., 1882, 980), but that it has the composition $C_{10}H_9O_3N_2Br$.

3-*Chloro*-5-*nitro*-2-*hydroxy*-1-*methyl*-1 : 2-*dihydroquinoline*, obtained in a similar manner, crystallises in yellow, glistening needles, darkens at 110°, and melts and decomposes at 120—130°. With alcohols, it yields a series of ethers, and, when oxidised, a quinolone. The hydroxydihydro-compounds can undergo decomposition according to the equation $2C_9NH_7Me{\cdot}OH = C_9NH_6MeO + C_9NH_8Me + H_2O$, and La Coste's analytical numbers probably refer to the mixture thus obtained.

The precipitates described by Hantzsch and Kalb (Abstr., 1900, i, 113) are not crystalline, but brittle resins. Although, on analysis, they yield figures which agree with the anhydro-formula, they have been proved to consist of a mixture of quinolone and dihydroquinoline derivatives.

Ordinary ether, which contains peroxides, readily oxidises the bases to quinolones. When a mixture of quinoline methiodide and alkali is extracted with ordinary ether, the whole of the carbon compound is extracted by the ether in the form of a quinolone in less than 10 minutes, and the titre of the aqueous solution is altered. When pure ether is employed, nothing is extracted, and the titre of the aqueous solution remains the same. It thus appears certain that both the carbinol and the ammonium base can undergo oxidation.

[With O. Eliasberg.]—When dihydromethylquinoline is mixed with *N*/2 sodium hydroxide (4 mols.) and distilled in steam, the complete operation being performed in the absence of air, the distillate yields with picric acid the insoluble methylquinolinium picrate melting at 164°.

When quinoline methiodide is boiled with alkali, it yields the following among other products: salts of methylquinolinium, methyldihydroquinoline, methylquinolone, which are soluble in acids, and may be extracted by the aid of hydrochloric acid, and, in addition, oily frac-

tions consisting of quinoline and alkylquinolones, probably produced by the oxidation of alkylated 1 : 2-hydroquinoline during oxidation.

J. J. S.

Asymmetric Quaternary Ammonium Salts of the Tetrahydro*iso*quinoline Series. EDGAR WEDEKIND and ROBERT OECHSLEN (*Ber.*, 1903, 36, 1158—1163. Compare Abstr., 1902, i, 118).—From 2-benzyltetrahydro*iso*quinoline and ethyl iodoacetate, the same *ethyl benzyltetrahydro*iso*quinolinium-2-acetate iodide*,

$$\begin{matrix} CH_2-CH_2 \\ | \\ C_6H_4\cdot CH_2 \end{matrix}\!\!>NI(CH_2Ph)\cdot CH_2\cdot CO_2Et,$$

is obtained as from ethyltetrahydro*iso*quinoline-2-acetate and benzyl iodide; it crystallises from acetone, melts at 149°, and decomposes at 154—155°.

*Ethyl 2-phenacyltetrahydro*iso*quinolinium-2-acetate bromide*,

$$\begin{matrix} CH_2-CH_2 \\ | \\ C_6H_4\cdot CH_2 \end{matrix}\!\!>NBr(CH_2Bz)\cdot CH_2\cdot CO_2Et,$$

can be prepared only in one way, namely, from phenacyl bromide and ethyl 2-tetrahydro*iso*quinolineacetate; it forms colourless, microscopic crystals and decomposes at 89—90°. The interaction of ethyl bromoacetate with 2-phenacyltetrahydro*iso*quinoline fails to give a definite product.

*Ethyl tetrahydro*iso*quinoline-2-acetate*, $\begin{matrix} CH_2-CH_2 \\ | \\ C_6H_4\cdot CH_2 \end{matrix}\!\!>N\cdot CH_2\cdot CO_2Et$, obtained by mixing tetrahydro*iso*quinoline and ethyl chloroacetate, boils at 184—185° under 16 mm. pressure.

*2-Phenacyltetrahydro*iso*quinoline*, $C_9NH_{10}\cdot CH_2\cdot COPh$, prepared from ω-bromoacetophenone and tetrahydro*iso*quinoline, crystallises from alcohol in yellow needles and melts at 100—101°.

The *oxalate*, $C_9NH_{10}\cdot C_7H_7,H_2C_2O_4$, of 2-benzyltetrahydro*iso*quinoline crystallises from a mixture of alcohol and ether in colourless needles and melts at 198°.

W. A. D.

Diacid Asymmetric Ammonium Bases and a New Isomerism of Nitrogen. EDGAR WEDEKIND [with ROBERT OECHSLEN] (*Ber.*, 1903, 36, 1163—1169. Compare Abstr., 1902, i, 643).—It has already been shown that ethyl 2-ethylenebistetrahydro*iso*quinolinium-2-acetate iodide, $C_2H_4\left[\cdot NI(CH_2\cdot CO_2Et)<\begin{matrix} CH_2\cdot C_6H_4 \\ | \\ CH_2\cdot CH_2 \end{matrix}\right]_2$ [not 1-acetate as stated in the former abstract], obtained by warming together ethyl iodide and ethyl tetrahydro*iso*quinoline-2-acetate (preceding abstract), completely differs from the *compound* prepared by the interaction of ethyleneditetrahydro*iso*quinoline (*infra*) with ethyl iodoacetate. Neither of the forms is convertible into the other.

A corresponding pair of isomerides is obtained by the interaction of ethylene iodide with 2-methyltetrahydroquinoline (kairoline), and by the combination of methyl iodide with ethyleneditetrahydroquinoline. The isomerism is probably due to the presence of two asymmetric nitro-

gen atoms, and is thus similar to that which exists between racemic and mesotartaric acids.

*Ethyleneditetrahydro*iso*quinoline*, $C_2H_4\left[\cdot N<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot C_6H_4\end{matrix}\right]_2$, obtained by the interaction of ethylene bromide with tetrahydro*iso*quinoline, crystallises from light petroleum in rhombohedra and melts at 95—96°. W. A. D.

Ammonium Compounds. HERMAN DECKER and H. ENGLER (*Ber.*, 1903, 36, 1169—1177).—From a consideration of their properties, the authors consider that 1-methylquinolone and the anhydride of 6-hydroxy-1-methylquinolinium hydroxide (Claus and Howitz, Abstr., 1891, 1252; 1898, 274) belong to two different classes; the former is probably $C_6H_4<\begin{matrix}CH{=}CH\\ NMe\cdot CO\end{matrix}$, and the latter a bimolecular anhydride, $C_9H_6<\begin{matrix}NMe\cdot O\\ O\cdot NMe\end{matrix}>C_9H_6$.

6-*Amino*-1-*methyl*-2-*quinolone*, $C_{10}H_{10}ON_2$, obtained by reducing 6-nitro-1-methyl-2-quinolone with alcoholic ammonium sulphide, separates from benzene in yellow crystals, melts at 165°, and gives a *hydrochloride* crystallising in needles and melting at 277°; the *acetyl* derivative is obtained from water or alcohol in silky crystals and melts at 278—281°.

6-*Ethoxy*-1-*methyl*-2-*quinolone* (*quinphenetolmethylquinolone*), obtained by the action of alkaline potassium ferricyanide on the corresponding methiodide, crystallises from a mixture of benzene and light petroleum in colourless, triclinic plates [$a:b:c = 3\cdot09096:1:1\cdot42005$; $\alpha = 108°34'$, $\beta = 74°6'$, $\gamma = 89°40'$] and melts at 116°; the *hydrochloride* crystallises in colourless needles and melts and decomposes at 150°. It is easily reduced by hydriodic acid to 6-hydroxy-1-methyl-2-quinolone (Howitz and Bärlocher, this vol., i, 279), which always crystallises with $1H_2O$ and melts at 228°.

6-*Quinanisolethiodide* (6-*methoxyquinoline ethiodide*) crystallises from water in yellow plates with $1H_2O$ and melts, when anhydrous, at 179°. By alkaline potassium ferricyanide, it is converted into 6-*methoxy*-1-*ethyl*-2-*quinolone*, a yellow oil which cannot be made to crystallise; the *hydrochloride* melts at 165°, and the *platinichloride* decomposes at 180°.

8-*Hydroxy*-1-*methyl*-2-*quinolone*, obtained by the action of hydriodic acid on 8-methoxy-1-methyl-2-quinolone (Fischer, this vol., i, 52), crystallises from water, sublimes in snow-white leaflets and melts at 286°. 8-*Hydroxy*-1-*ethyl*-2-*quinolone*, prepared similarly, melts at 202—203°. W. A. D.

Asymmetric Alkylated Diaminoacridine Dyes. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 133709).—Asymmetric di- or tri-alkylated tetraminodiphenylmethane bases are prepared by the condensation of 1 mol. of formaldehyde with 1 mol. of an *as*-dialkylated *m*-diamine and 1 mol. of an *m*-diamine or monoalkyl-*m*-

diamine. They are colourless, crystalline substances, insoluble in water but soluble in toluene, chloroform, alcohol, or dilute acids.

Dimethyltetraminodiphenylmethane crystallises from toluene,

$$NMe_2\cdot C_6H_3(NH_2)\cdot CH_2\cdot C_6H_3(NH_2)_2,$$

and melts at 188—190°. *Dimethyltetraminophenyl*-o-*tolylmethane*, $NMe_2\cdot C_6H_3(NH_2)\cdot CH_2\cdot C_6H_2Me\cdot(NH_2)_2$, crystallises from chloroform in leaflets melting at 177°. *Trimethyltetraminodiphenylmethane*, $NMe_2\cdot C_6H_3(NH_2)\cdot CH_2\cdot C_6H_3(NH_2)\cdot NHMe$, and *trimethyltetraminophenyl*-o-*tolylmethane*, $NMe_2\cdot C_6H_3(NH_2)\cdot CH_2\cdot C_6H_2Me(NH_2)\cdot NHMe$, crystallise from toluene and melt respectively at 95° and 155°. *Diethyltetraminophenyl*-o-*tolylmethane*, $NEt_2\cdot C_6H_3(NH_2)\cdot CH_2\cdot C_6H_2Me(NH_2)_2$, granular crystals from alcohol, melts at 122°.

On heating with water, especially with addition of acids or of zinc chloride, ammonia is eliminated and the corresponding acridine leuco-bases are formed. These are readily oxidised to the dyes by atmospheric oxygen or ferric chloride. The products are all soluble in water with an orange-yellow colour. Their solutions in dilute alcohol show a fine green fluorescence. C. H. D.

Acridine Syntheses from Aldehydes and Aromatic Bases. FRITZ ULLMANN (*Ber.*, 1903, 36, 1017—1027. Compare Haase, this vol., i, 366)—[With M. WAITZ].—Aromatic bases having an alkyl group in the para-position relative to the amino-group form, with aldehydes, methylene derivatives, $C_6H_4Me\cdot N\colon CH_2$, which, on heating with excess of the base or its hydrochloride, yield an *o*-diaminodiphenylmethane derivative, $CH_2(C_6H_3Me\cdot NH_2)_2$; the latter loses ammonia forming 2 : 7-dimethylhydroacridine, $C_6H_3Me<\substack{CH_2\\NH}>C_6H_3Me$, and is then oxidised to an acridine derivative. Thus, 2 : 7-dimethylacridine, $C_6H_3Me<\substack{CH\\|\\N}>C_6H_3Me$, is formed from formaldehyde and *p*-toluidine; this substance, which can also be prepared by oxidising the corresponding hydroacridine with ferric chloride, melts at 171° (corr.); the alcoholic solution has a blue fluorescence; the *nitrate* crystallises in yellow needles and the *platinichloride* forms an insoluble, crystalline powder, and the *dichromate* a dark yellow, crystalline powder. 2 : 7-*Dimethylhydroacridine* which is formed together with methylacridine, crystallises in needles melting at 218—220°.

[With N. WEINTRAUB.]—9-*Phenyl*-2 : 7-*dimethylacridine*,

$$C_6H_3Me<\substack{CPh\\|\\N}>C_6H_3Me,$$

is produced together with dimethylphenylhydroacridine as the result of a series of changes similar to those just described, when benzaldehyde is heated with a mixture of toluidine and toluidine hydrochloride; it crystallises in pale yellow needles melting at 172° (compare Meyer, Abstr., 1899, i, 945). The *dichromate* forms orange-yellow, insoluble crystals.

9-*Phenyl*-2 : 7-*dimethylhydroacridine* forms colourless needles, has no basic properties, and reduces silver nitrate.

9-*Phenyl*-2 : 4 : 5 : 7-*tetramethylacridine* is prepared from *m*-xylidine

and benzaldehyde, crystallises in pale yellow needles melting at 152°, and has a green fluorescence in acetic acid solution.

p-*Nitrobenzylidene*-p-*toluidine*, prepared by mixing *p*-nitrobenzaldehyde and *p*-toluidine in concentrated alcoholic solution, crystallises in yellow leaflets melting at 124·5°, and is identical with Bischler's β-nitrophenyldiamino-*p*-tolylmethane (Abstr., 1889, 132), which can therefore no longer be regarded as a triphenylmethane derivative. When heated with *p*-toluidine hydrochloride, 4′-*nitro*-2″ : 2‴-*diamino*-5″ : 5‴-*dimethyltriphenylmethane* is obtained as pale yellow needles melting at 172°, and is identical with Bischler's α-*p*-nitrophenyldiaminotolylmethane.

9-p-*Nitrophenyl*-2 : 7-*dimethylacridine*,

$$C_6H_3Me<\begin{matrix}C(C_6H_4\cdot NO_2)\\ | \\ N\text{------------}\end{matrix}>C_6H_3Me,$$

is formed when *p*-toluidine and *p*-toluidine hydrochloride are heated with *p*-nitrobenzylidene-*p*-toluidine, and is obtained in small, brown leaflets or crystals melting at 265°; at the same time, there is always produced by intramolecular reduction 9-p-*aminophenyl*-2 : 7-*dimethylacridine*, which crystallises in yellow needles melting at 268°, and dissolves in acids with an orange-yellow coloration.

m-*Nitrobenzylidene*-p-*toluidine* crystallises in pale yellow needles melting at 96°. 3′-*Nitro*-2″ : 2‴-*diamino*-5″ : 5‴-*dimethyltriphenylmethane*, prepared as the corresponding *p*-nitro-derivative, crystallises in yellow needles melting at 183° (compare Bischler, *loc. cit.*). 9-m-*Nitrophenyl*-2 : 7-*dimethylacridine* crystallises in brown needles melting at 268°, the corresponding *amino*-derivative in yellow needles melting at 273°; the *acetyl* derivative of the latter forms pale yellow needles melting at 280°.

[With B. MÜHLHAUSER.]—6-*Amino*-2 : 7-*dimethylacridine*,

$$NH_2\cdot C_6H_2Me<\begin{matrix}CH\\ | \\ N\text{--}\end{matrix}>C_6H_3Me,$$

is prepared by adding tetra-aminoditolylmethane and *p*-toluidine hydrochloride successively to molten *p*-toluidine, and then heating the mixture at 160—170°; the base crystallises in yellowish-brown crystals melting at 244°, and has a green or bluish-green fluorescence in various solvents; the *hydrochloride* crystallises in red needles; the *acetyl* derivative is a pale yellow, crystalline powder melting at 258°.

K. J. P. O.

Naphthacridines. FRITZ ULLMANN and A. FETVADJIAN (*Ber.*, 1903, 36, 1027—1031. Compare Abstr., 1900, i, 360, 361, 689).—Instead of the prefixes α-, β-, to denote the various isomeric naphthacridines, it is suggested that they should be distinguished by the numerals which indicate the carbon atoms in the two naphthalene nuclei, directly connected with the group $\begin{matrix}-CH-\\ | \\ -N-\end{matrix}$. Thus, the so-called β-naphthacridine becomes 1 : 2 : 1′ : 2′-naphthacridine.

β-Naphthacridine, $C_{10}H_6<\begin{matrix}CH\\ | \\ N\text{--}\end{matrix}>C_{10}H_6$, can be obtained in various

ways, but it is best prepared by heating together β-naphthylamine, β-naphthol, and trioxymethylene; it crystallises in pale yellow needles melting at 216°; the *nitrate* forms yellow, insoluble needles.

1 : 2 : 2′ : 1′-*Naphthacridine* is prepared from β-naphthol and α-naphthylamine, forms pale yellow crystals melting at 228°, and dissolves in alcohol with a yellow coloration and an intense blue fluorescence the *nitrate* crystallises in orange-yellow needles and the *hydrochloride* in small needles.

[With N. Racovitza.]—9-Phenyl-β-naphthacridine is prepared by heating together benzaldehyde, β-naphthylamine, and β-naphthol, when the dihydro derivative is formed, having the properties and melting point (230°) ascribed to it by Haase (this vol., i, 366); on oxidation with bromine, it is converted into the acridine melting at 297° (compare Claus and Richter, Abstr., 1884, 1358; Ris, Abstr., 1884, 1357).

9-*Phenyl*-1 : 2 : 2′ : 1′-*hydronaphthacridine*, prepared after the same manner as the compound last mentioned, crystallises in colourless needles melting at 240° and is oxidised by bromine to the corresponding *acridine*, which forms pale yellow crystals melting at 254°; both these compounds yield solutions exhibiting a strong, blue fluorescence; the *hydrobromide* of the latter forms orange-yellow crystals, and the *nitrate*, orange-yellow leaflets. K. J. P. O.

Some Aldehyde Condensation Products of Aryl-ψ-thiohydantoins. Henry L. Wheeler and George S. Jamieson (*J. Amer. Chem. Soc.*, 1903, **25**, 366—371).—The authors had previously observed (Abstr., 1902, i, 758) that certain stable ψ-thiohydantoins yield diacetyl derivatives, the behaviour of which indicates that the grouping $CO{\cdot}CH_2{\cdot}S$ is not present in the original hydantoins. Andreasch has shown (Abstr., 1888, i, 47) that ψ-thiohydantoin condenses with benzaldehydes as if it contained the above grouping. It is now found that substituted ψ-thiohydantoins condense with aldehydes and ethyl oxalate in analogous manner.

2-*Phenylimino-4-keto-5-benzylidenetetrahydrothiazole*,

$$CHPh{:}C{<}\begin{matrix}S-C{:}N{\cdot}Ph\\ \quad\;\; | \\ CO{\cdot}NH\end{matrix},$$

prepared by condensing phenyl-ψ-thiohydantoin and benzaldehyde, crystallises from alcohol in light yellow prisms melting at about 251—252°. It forms an additive compound with sodium ethoxide, $C_{16}H_{12}ON_2S{\cdot}NaOEt$, a bright yellow, crystalline powder which melts at about 263° and yields, with benzyl chloride, *phenylbenzyl-5-benzylidene-ψ-thiohydantoin*, $CHPh{:}C{<}\begin{matrix}S-C{\cdot}NPh{\cdot}CH_2Ph\\ \quad\;\; \| \\ CO{\cdot}N\end{matrix}$, melting at 186—187°.

Piperonalphenyl-ψ-thiohydantoin, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}C{<}\begin{matrix}S-C{:}NPh\\ \quad\;\; | \\ CO{\cdot}NH\end{matrix}$, from phenyl-$\psi$-thiohydantoin and piperonal, forms bright yellow, crystals melting at about 259—261°.

Phenyl-m-*nitrobenzylidene-ψ-thiohydantoin* is a brick-red, crystalline powder.

2 : 3-*Di* o-*tolyl-ψ-thiohydantoin*, $CH_2<\begin{matrix}S—C:N\cdot C_7H_7\\ CO\cdot N\cdot C_7H_7\end{matrix}$, prepared from di-*o*-tolylthiocarbamide and chloroacetic acid, separates in flat prisms melting at 151—152°. Its *benzylidene* derivative crystallises in light yellow prisms melting at 179—180° and forms a sodium ethoxide additive product, $C_{24}H_{20}ON_2S\cdot NaOEt$.

p-*Dimethylaminophenylthiocarbamide*, $NH_2\cdot CS\cdot NH\cdot C_6H_4\cdot NMe_2$, prepared from dimethyl-*p*-phenylenediamine hydrochloride and ammonium thiocyanate, forms a pale yellow powder which melts and decomposes at 180—181°; when warmed with ammonium chloroacetate, it gives p-*dimethylaminophenylthiohydantoic acid*, which, on warming with glacial acetic acid, yields p-*dimethylaminophenyl-ψ thiohydantoin*, $CH_2<\begin{matrix}S—C:N\cdot C_6H_4\cdot NMe_2\\ CO\cdot NH\end{matrix}$, a dull yellow powder which sinters at about 210° and melts at 222°. This latter substance condenses with *p*-nitrobenzaldehyde to give p-*nitrobenzylidene*-p-*dimethylaminophenyl-ψ-thiohydantoin*, which melts at about 250—252°.

Phenyl-ψ-thiohydantoinglyoxylic acid, $CO_2H\cdot CO\cdot CH<\begin{matrix}S—C:NPh\\ CO\cdot NH\end{matrix}$, from phenyl-ψ-thiohydantoin and ethyl oxalate, forms yellow crystals which melt and decompose at about 221—222°. A. McK.

[Formyl Derivatives of Aromatic Bases.] ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R GEIGY (D.R.-P. 138839).—*m*-Tolylenediamine is boiled with 1 or 2 mols. of formic acid, and after cooling the product is recrystallised from hot water.

Formyl-m-*tolylenediamine* forms transparent pyramids, slightly soluble in cold water, melting at 113—114°. *Diformyl*-m-*tolylenediamine* crystallises from hot water in bunches of white needles, melting at 176—177°.

Formyl-2-nitro-p-*toluidine* crystallises from hot water in fine white, very voluminous needles which melt at 133—134°. *Formyl-4-nitro*-o-*toluidine* forms small, yellow prisms melting at 178—179°.

C. H. D.

The Chloride of Benzaldehydephenylhydrazone-*N*-carboxylic Acid. MAX BUSCH and AUGUST WALTER (*Ber.*, 1903, 36, 1357—1362).—A benzene solution of benzaldehydephenylhydrazone reacts with a toluene solution of carbonyl chloride in the presence of pyridine yielding the *chloride* of *benzaldehydephenylhydrazone*-N-*carboxylic acid*, $COCl\cdot NPh\cdot N:CHPh$. It crystallises in long, glistening plates, melts at 101—102°, and dissolves readily in most organic solvents. When its alcoholic solution is shaken with aqueous ammonia, *benzaldehyde-2-phenylsemicarbazone*, $NH_2\cdot CO\cdot NPh\cdot N:CHPh$, is obtained in the form of colourless, flat, glistening needles melting at 154° and soluble in most organic solvents. When hydrolysed with 20 per cent. sulphuric acid and alcohol, it yields 2-*phenylsemicarbazide*, $NH_2\cdot CO\cdot NPh\cdot NH_2$, which crystallises from benzene in flat needles melting at 118—119° and readily soluble in alcohol or warm water. The *hydrochloride*, $C_7H_9ON_3,HCl$, crystallises in compact, colourless plates, melts and

decomposes at 185—186°, and is readily soluble in water. The base differs from the isomeric 1-phenylsemicarbazide (Fischer, Abstr., 1878, 307) in its more pronounced basic properties and in the fact that it is not oxidised by ferric chloride and does not give Bülow's reaction. When heated for half an hour at 160°, it is partially transformed into its isomeride, but is also decomposed to a slight extent.

Benzaldehyde-2 : 4-*diphenylsemicarbazone*, NHPh·CO·NPh·N:CHPh, obtained by the action of benzaldehyde on the chloride already described, crystallises from alcohol in colourless needles melting at 173°. On oxidation with ferric chloride, it yields 1 : 3 : 4-*triphenyl*-1 : 2 : 4-*triazolone*, $NPh<\begin{matrix} CPh:N \\ CO-NPh \end{matrix}$, melting at 215—216°. When the diphenylsemicarbazone is boiled with alcohol and 20 per cent. sulphuric acid for 1·5 hours, it yields a small amount of 2 : 4-*diphenylsemicarbazide*, NH_2·NPh·CO·NHPh, in the form of glistening plates melting at 165°. It has pronounced basic properties, and at its melting point is transformed into the isomeric 1 : 4-derivative.

Benzylidene-2 : 5 *diphenylsemicarbazide*,

CHPh:N·NPh·CO·NH·NHPh,

obtained by the action of phenylhydrazine on the chloride of benzaldehydephenylhydrazonecarboxylic acid, crystallises in glistening needles and melts at 206—207°. J. J. S.

Constitution of Porphyrexide, an Analogue of Isatin. OSCAR PILOTY and WILHELM VOGEL (*Ber.*, 1903, 36, 1283—1304).—The formula $NH_2\cdot C(CN)<\begin{matrix} CMe_2 \\ NH \end{matrix}>N\cdot OH$ for porphyrexine (Abstr., 1901, 517, 583) is improbable (1) because amidines do not unite with hydrogen cyanide in this way, (2) because no indication can be obtained of the presence of a nitrilic group. The substance is therefore formulated as a 2 : 4-*di-imino*-1-*hydroxy*-5 : 5-*dimethylhydantoin*, $\begin{matrix} CMe_2\cdot N(OH) \\ C(:NH)-NH \end{matrix}>C:NH$, and the thio-derivative (*loc. cit.*) as

$$\begin{matrix} CMe_2\cdot N(OH) \\ C(:NH)-NH \end{matrix}>CS.$$

Acids and alkalis hydrolyse the substance to a *base*, which is formulated as $\begin{matrix} CMe_2\cdot N(OH) \\ C(:NH)-NH \end{matrix}>CO$; this separates from alcohol with $1C_2H_6O$ in long, silky, monoclinic needles and melts and decomposes at 230°; like porphyrexine, it was oxidised by alkaline potassium ferricyanide to a very unstable brown compound, which detonated when heated to 75° and decomposed before it could be analysed; the *sulphate* crystallises in long needles and melts at 245°; the hydrochloride has already been obtained by the action of hydrochloric acid on porphyrexide. An isomeric *monochloroporphyrexide* was prepared by the action of hypochlorite on porphyrexide; this forms minute, red prisms, melts at 151·5°, and is converted by further chlorination into the dichloro-derivative already prepared from the isomeric monochloroporphyrexide; in each case, the imino-group is chlorinated, and the chlorine is

readily removed in the form of hypochlorous acid. The product of hydrolysis described above is reduced electrolytically to 4-*imino*-5 : 5-*dimethylhydantoin*, $\begin{matrix}\mathrm{CMe}\text{——}\mathrm{NH}\\ \mathrm{C(:NH)\cdot NH}\end{matrix}\!>\!\mathrm{CO}$, which crystallises in rhombic forms, with $1H_2O$, sinters and loses water at 110—130°, and melts and decomposes at 230°.

A close resemblance exists between porphyrexide, formulated as $\begin{matrix}\mathrm{Me_2C\cdot NO}\\ \mathrm{NH{:}C\cdot NH}\end{matrix}\!>\!\mathrm{C{:}NH}$, and isatin, $\begin{matrix}\mathrm{CH\cdot CH{:}C{-}CO}\\ \mathrm{CH\cdot CH{:}C\cdot NH}\end{matrix}\!>\!\mathrm{CO}$, the $>$NO group (quadrivalent nitrogen) taking the place of one of the $>$CO groups. The analogy is shown not only in physical properties, but to a slight extent in chemical properties. Aqueous alkalis convert porphyrexide into a *compound*, $C_5H_{10}ON_4$, formulated as

$$\mathrm{NO\cdot CMe_2\cdot C(NH)\cdot NH\cdot CH{:}NH},$$

which forms a colourless, crystalline powder and melts and decomposes at 160°; like other nitroso-compounds (Bamberger and Seligman, this vol., i, 322), it dissolves in acetic acid to a blue solution; the *sodium* salt, $C_5H_9N_4ONa,4H_2O$, crystallises in silky needles. The nitroso-compound is reduced by sodium amalgam to a *reduction* product, $C_5H_9N_4$, which forms prismatic flakes and melts and decomposes at 147°; its *sodium* salt, when warmed, is converted into a *compound*, $C_5H_9ON_3$, which crystallises in short, stout prisms and melts and decomposes at 140°.

By the action of hydrazine hydrate on porphyrexine, a *hydrazone*, $\mathrm{N_2}\left[\mathrm{C}\!<\!\begin{matrix}\mathrm{N(OH)\cdot CMe_2}\\ \mathrm{NH\text{——}C{:}NH}\end{matrix}\right]_2$, is produced, which forms yellow flakes and melts and decomposes at 280°; the *tetra-acetyl* derivative, $C_{18}H_{26}O_6N_8$, crystallises from ethyl acetate in stout, pointed, silky prisms and melts and decomposes at 178°. The hydrazone is oxidised by potassium ferricyanide to a *porphyrindine* formulated as

$$\mathrm{N_2}\left[\mathrm{{:}C}\!<\!\begin{matrix}\mathrm{NO{-}CMe_2}\\ \mathrm{NH\cdot C{:}NH}\end{matrix}\right]_2;$$

this, the analogue of porphyrexide, crystallises in dark blue, stout prisms with $2H_2O$ and melts and intumesces at 190°. The *diacetyl* derivative, $C_{14}H_{20}O_4N_8$, prepared by the action of chlorine on the preceding tetra-acetyl compound, forms a dark blue, crystalline powder, which melts and decomposes at 170°. T. M. L.

Condensation Products of ψ-Thiocarbamides. Synthesis of Uracil, Thymine, and Similar Compounds. Henry L. Wheeler and Henry F. Merriam (*Amer. Chem. J.*, 1903, 29, 478—492).—ψ-Thiocarbamides are strongly basic; they are in general more reactive and undergo condensations more readily than the normal thiocarbamides.

2-*Methylthiol*-6-*oxypyrimidine*, $\mathrm{NH}\!<\!\begin{matrix}\mathrm{C(SMe){:}N}\\ \mathrm{CO\text{——}CH}\end{matrix}\!>\!\mathrm{CH}$, prepared by the action of ψ-methylthiocarbamide hydriodide on ethyl sodioformylacetate, crystallises from water in long prisms or lozenge-shaped

tablets and melts at 198—199°. 2-*Ethylthiol*-6-*oxypyrimidine*, prepared in an analogous manner, forms colourless, stout prisms and pyramids melting at 152°. When heated in a sealed tube with concentrated hydrochloric acid, it yields uracil, which was also obtained from the methyl homologue. The uracil, so prepared, crystallises in white needles, melts at 338°, and agrees in properties with the uracil prepared by E. Fischer and Roeder (Abstr., 1902, i, 124) from the bromo-derivatives of hydrouracils. When bromine is added to a solution of uracil in carbon disulphide, 5-*bromouracil* is produced; it crystallises from water in stout prisms which melt and decompose at about 293°.

2-*Methylthiol*-4-*methyl*-6-*oxypyrimidine*, prepared by the action of ψ-methylthiocarbamide hydriodide on ethyl acetoacetate in aqueous potassium hydroxide solution, forms long prisms melting at 219°, and when boiled with hydrobromic acid yields 4-methyluracil.

2-*Methylthiol*-5-*methyl*-6-*oxypyrimidine*, from ψ-methylthiocarbamide hydriodide and ethyl sodioformylpropionate, crystallises from water in small plates which sinter at about 225° and melt at 233°. When boiled with hydrochloric acid until no more mercaptan is evolved, it gives a quantitative yield of 5-*methyluracil* (thymine),

$$NH<\begin{matrix}CO\cdot CMe\\CO-NH\end{matrix}>CH;$$

this crystallises from water in plates, which, on being rapidly heated, melted at 326°. The thymine, so prepared, was found to be identical with the natural product obtained from the nucleic acid of the spleen.

2-*Ethylthiol*-4:5-*dimethyl*-6-*oxypyrimidine*, prepared from ψ-ethylthiocarbamide hydrobromide and ethyl methylacetoacetate in aqueous potassium hydroxide solution, forms stout prisms which sinter at 151° and melt at about 156°. When treated with hydrochloric acid, it yields 4:5-*dimethyluracil*, crystallising from alcohol in microscopic needles which melt and decompose at 292°.

2-*Methylthiol*-4-*methyl*-5-*ethyl*-6-*oxypyrimidine*, prepared from ψ-methylthiocarbamide hydriodide and ethyl ethylacetoacetate in aqueous potassium hydroxide solution, separates from alcohol in flat prisms with brush-like ends and melts at 201—203° with slight effervescence. The 4-*methyl-5-ethyluracil*, obtained from it, crystallises in leaflets melting at 237°.

2-*Methylthiol*-4-*phenyl*-6-*oxypyrimidine*, prepared from ψ-methylthiocarbamide hydriodide and ethyl benzoylacetate in aqueous potassium hydroxide solution, forms long, slender needles melting at 240°. The 4-*phenyluracil*, obtained from it, forms microscopic prisms melting at 269—270°. The phenyluracil of E. Fischer and Roeder melted at 267° (corr.). When aminoacetic acid is added to an aqueous solution of ψ-methylthiocarbamide hydriodide and potassium hydroxide, guanidineacetic acid (glycocyamine) is formed; this crystallises in rectangular plates which decompose at 250—260°. The *picrate* melts and decomposes at about 202°. *Orthoguanidine benzoic acid* was prepared from ψ-methylthiocarbamide hydriodide and anthranilic acid.

ψ-*Methylthiocarbamide chloroacetate*, prepared from ψ-methylthio-

carbamide hydriodide and chloroacetic acid, crystallises from alcohol in rectangular plates melting at 162°. A. McK.

Syntheses of Amino-oxypyrimidines having the Composition of Cytosine; 2-Amino-6-oxypyrimidine and 6-Amino-2-oxypyrimidine. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1903, 29, 492—504. Compare preceding abstract).—Kossel and Steudel (this vol., i, 303) obtained from sturgeon's testicles a basic substance closely resembling cytosine and having the formula $C_4H_5ON_3$, and conclude (this vol., ii, 311) that this product is identical with thymus cytosine. The same base may also be prepared from the nucleic acid of the pancreas and the spleen (Levene, this vol., i, 375). The authors have prepared the isomeric 6-amino-2-oxypyrimidine and 2-amino-6-oxypyrimidine, and incline to the view that the former is identical with cytosine.

6-*Chloro-2-ethylthiolpyrimidine*, $N\lessgtr\begin{matrix}C(SMe){:}N\\CCl{-}{-}CH\end{matrix}\gtrless CH$, was prepared by the action of phosphorus pentachloride on 2-ethylthiol-6-oxypyrimidine; it is an oil, stable at 150°, and when boiled with hydrochloric acid gives uracil. When heated with alcoholic ammonia, 6-*amino-2-ethylthiolpyrimidine* is formed; it separates as colourless plates melting at 85—86°. When boiled with hydrobromic acid until no more mercaptan was evolved, 6-*amino-2-oxypyrimidine*,

$$N\lessgtr\begin{matrix}CO{-}{-}{-}NH\\C(NH_2){\cdot}CH\end{matrix}\gtrless CH,$$

is formed; this separates from water in needle-like prisms containing $1H_2O$ and melting and decomposing at 320—325°. Its *picrate* decomposed at about 300—305°. Its *acetyl* derivative crystallises in microscopic prisms, whilst its *phenylcarbimide* derivative melts and decomposes at 260°.

2-*Amino-6-oxypyrimidine*, $NH\lessgtr\begin{matrix}C(NH_2){:}N\\CO{-}{-}{-}CH\end{matrix}\gtrless CH$, prepared by dissolving guanidine carbonate in barium hydroxide solution and then adding ethyl sodioformylacetate, separates from water either as prisms or as silky needles and decomposes at about 276°. When it is heated with sulphuric acid, uracil is formed. The *picrate* begins to decompose at 255°, and the *platinichloride* at 200°. The *acetyl* derivative crystallises from alcohol in nacreous scales melting at 247°. 5-*Bromo-2-amino-6-oxypyrimidine* crystallises in radiating masses of pointed plates; its *hydrobromide* forms needle-like prisms melting and decomposing at about 273°. A. McK.

Cytosine or 6-Amino-2-oxypyrimidine from Tritico-nucleic Acid. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1903, 29, 505—511. Compare preceding abstract).—It has been shown by Osborne and Harris (Abstr., 1902, i, 847) that wheat embryos contain a nucleic acid from which uracil can be obtained. The mother liquors, from which the uracil had been removed by Osborne and Harris, were examined by the authors, who isolated from them a mixture of about equal parts of uracil and cytosine. The picrate

prepared from this mixture appeared to be identical with the picrate of thymus cytosine described by Kossel and Steudel (this vol., ii, 311), and yielded a base identical with the synthetical 6-amino-2-oxypyrimidine of the authors. The crystalline forms of the synthetical cytosine and the wheat cytosine platinichlorides are described; they are identical with one another and with the platinichloride of Levene's cytosine from spleen. One hundred parts of water at 25° dissolve 0·83 part of wheat cytosine, 0·78 of spleen cytosine, and 0·79 part of synthetical cytosine respectively. The cytosine prepared from the three sources is therefore identical. A. McK.

Preparation of Theophylline and its Alkali-derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 138144).—Theophylline has been prepared by Traube (Abstr., 1900, i, 416) by heating the formyl derivative of 4 : 5-diamino-1 : 3-dimethyl-2 : 6-dihydroxypyrimidine. It is found that the reaction is more conveniently carried out, and at a lower temperature, by warming the formyl derivative with an aqueous or alcoholic solution of alkali hydroxide on a water-bath. The alkali salt loses water to form the corresponding derivative of theophylline. C. H. D.

Synthesis of Alkylthioketodihydroquinazolines from Anthranilonitrile. MARSTON T. BOGERT, H. C. BRENEMAN and W. F. HAND (*J. Amer. Chem. Soc.*, 1903, 25, 372—380).—Bogert and Hand have shown (this vol., i, 202) that alkylketodihydroquinazolines can be prepared from acyl-*o*-aminobenzonitriles by the action of warm alkaline hydrogen peroxide solution or by heating in sealed tubes with acid anhydrides. The preparation of the corresponding thioquinazolines is now described; these compounds represent a new type of thioquinazolines in so far that the sulphur atom is attached to the carbon adjacent to the benzene nucleus, whilst in the thioquinazolines described by other authors the sulphur is attached to the carbon between the two nitrogen atoms.

o-*Aminobenzothioamide*, prepared from *o*-aminobenzonitrile and alcoholic ammonia, crystallises in light yellow flakes or plates which melt at 121—122°. When boiled with acetic anhydride, it forms 4-*thion*-2-*methyldihydroquinazoline*, $C_6H_4{<}\begin{matrix}N{=}CMe\\ CS{\cdot}NH\end{matrix}$, which is prepared in larger yield from *o*-aminobenzonitrile by hydrogen sulphide, or by acetic anhydride and sodium sulphide, or by thioacetic acid; it crystallises in yellow needles or prisms, melting and decomposing at about 218—219°. Its *picrate* melts at 198·5—199·5°.

4-*Thion*-2-*ethyldihydroquinazoline*, prepared in analogous fashion, forms yellow needles melting and decomposing at about 203—204°. 4-*Thion*-2-iso*propyldihydroquinazoline*, from *o*-aminobenzonitrile, *iso*butyric anhydride, and sodium sulphide, crystallises from alcohol in light yellow needles melting at 203—204°. 4-*Thion*-2-n-*propyldihydroquinazoline* forms light yellow needles melting at 182—183°.

A. McK.

Wandering of a Methyl Group in Pyrazole Derivatives. LUDWIG KNORR (*Ber.*, 1903, 36, 1272—1274).—A change, involving the shifting of a methyl group, sometimes takes place in compounds containing a $>CMe_2$ group. The conversion of pinacone into pinacoline is the simplest instance, but three instances are quoted in the case of pyrazole derivatives: (1) the conversion of 5-hydroxy-1-phenyl-3 : 4 : 4-trimethylpyrazoline into 1-phenyl-3 : 4 : 5-trimethylpyrazole (Knorr and Jochheim, following abstract):

$$NPh<\begin{matrix}N\text{—}CH\cdot OH\\ CMe\cdot CMe_2\end{matrix} \rightarrow NPh<\begin{matrix}N\text{—}CMe\\ CMe\cdot CMe\end{matrix};$$

(2) the conversion of 1-phenyl-3-dimethylindolinole into 1-phenyl-2 : 3-dimethylindole (Brunner, Abstr., 1900, i, 360):

$$C_6H_4<\begin{matrix}CMe_2\\ NPh\end{matrix}>CH\cdot OH \rightarrow C_6H_4<\begin{matrix}CMe\\ NPh\end{matrix}>CMe;$$

(3) the conversion of 3 : 4 : 4 : 5-tetramethylpyrazole through the methiodide into 1 : 3 : 4 : 5-tetramethylpyrazole:

$$CMe_2<\begin{matrix}CMe{:}N\\ CMe{:}N\end{matrix} \rightarrow CMe<\begin{matrix}CMe\cdot N\\ CMe\cdot NMe\end{matrix}.$$

T. M. L.

5-Hydroxy-1-phenyl-3 : 4 : 4-trimethylpyrazoline and its Conversion into 1-Phenyl-3 : 4 : 5-trimethylpyrazole. LUDWIG KNORR and E. JOCHHEIM (*Ber.*, 1903, 36, 1275—1278).—5-*Hydroxy*-1-*phenyl*-3 : 4 : 4-*trimethylpyrazoline*, $NPh<\begin{matrix}CH(OH)\cdot CMe_2\\ N\text{=====}CMe\end{matrix}$, prepared by reducing the corresponding ketone with sodium and alcohol, crystallises from light petroleum and melts at 118°. When warmed with concentrated sulphuric or hydrochloric acid, it gives 1-*phenyl*-3 : 4 : 5-*trimethylpyrazole*, $NPh<\begin{matrix}CMe{:}CMe\\ N\text{===}CMe\end{matrix}$, the yield being from 70 to 80 per cent of the theoretical quantity; the pyrazole, which can be prepared synthetically from phenylhydrazine and methylacetylacetone, is a yellow oil of pleasant, aromatic odour, boils at 287—290° under 750 mm. pressure, and does not solidify in a freezing mixture; the *platinichloride* separates from hydrochloric acid in hexagonal crystals and decomposes, liberating hydrogen chloride, at 195—196°; the *aurichloride* forms yellow needles and melts at 133°; the *picrate* crystallises from alcohol and melts at 116°. T. M. L.

Pyrazoles from 1 : 3-Diketones and Alkyl Diazoacetates. AUGUST KLAGES and A. RÖNNEBERG (*Ber.*, 1903, 36, 1128—1132. Compare Abstr., 1902, i, 496).—The explanation given by Klages (*loc. cit.*) of the formation of pyrazoles in this reaction is shown to be in harmony with Hantzsch and Lehmann's observations (Abstr., 1901, i, 678), whilst that suggested by Wolff (this volume, i, 208) is not.

Methyl 5-*acetyl*-4-*methylpyrazole*-3-*carboxylate*,

$$CAc<\begin{matrix}NH\cdot N\\ CMe\text{--}\end{matrix}>C\cdot CO_2Me$$

obtained by condensing acetylacetone with methyl diazoacetate,

crystallises from water or alcohol in lustrous, colourless needles, melts at 152°, and furnishes crystalline alkali salts. The *acid* melts at 233°. The silver salt, when distilled under reduced pressure, yields *5-acetyl-4-methylpyrazole*, a colourless oil which distils at 160—161° under 26 mm. pressure, solidifies when cooled, and then melts at 102—103°. The *phenylhydrazone* crystallises from dilute alcohol in colourless needles and melts at 135—136°. On oxidation with alkaline permanganate, 5-acetyl-4-methylpyrazole is converted into the 4-methylpyrazole-5-carboxylic acid described by von Pechmann (Abstr., 1901, i, 167).

The *phenylhydrazone* of the corresponding ethyl ester (Klages, *loc. cit.*, Wolff, *loc. cit.*) crystallises in colourless needles, melts at 197—198°, and is soluble in alcohol, less so in benzene or light petroleum. The *semicarbazone* forms colourless needles, melts at 220—221°, and is soluble in acetic acid, less so in other organic solvents. The ethyl ester, when methylated, furnishes *ethyl 5-acetyl-1:4-dimethylpyrazole-3-carboxylate*, which separates from dilute alcohol in colourless crystals, melts at 80—81°, and is readily soluble in alcohol, ether, or benzene, less so in water. The *acid* crystallises in colourless needles and melts at 185—186°.

Ethyl 5-acetyl-1-ethyl-4-methylpyrazole-3-carboxylate, similarly prepared, crystallises in brilliant needles, melts at 57—58°, and has solubilities similar to those of its lower homologue. The free *acid* forms small, colourless needles and melts at 167—168°. T. A. H.

Ketopyrazolone. II. 1:3-Diphenyl-4-ketopyrazolone. Franz Sachs and Petre Becherescu (*Ber.*, 1903, **36**, 1132—1138. Compare Sachs and Barschall, Abstr., 1902, i, 503).—*p*-Nitrosodimethylaniline condenses with 1:3-diphenylpyrazolone to form the 4-*p-dimethylaminoanil* of 1:3-diphenyl-4-ketopyrazolone,

$$\begin{matrix} N{=}CPh \\ | \\ NPh{\cdot}CO \end{matrix}\!\!>C{:}N{\cdot}C_6H_4{\cdot}NMe_2;$$

this crystallises in steel-blue needles, melts at 218·5°, and by dilute sulphuric acid is hydrolysed to 1:3-*diphenyl-4-ketopyrazolone*, $N{<}\begin{matrix} CPh{-}CO \\ \quad\ | \\ NPh{\cdot}CO \end{matrix}$, which crystallises in black needles, melts at 165°, and dissolves in sulphuric acid to a blood-red solution. The *alcoholate* forms groups of yellow-brown needles, the *hydrate* crystallises in colourless needles and loses a molecule of water at 82°; the *sodium bisulphite* compound crystallises in long, white needles, the *oxime* separates in yellow needles from dilute alcohol and melts at 200°; the *semicarbazone* forms dark red scales, sinters at 194°, and melts at 205·5°; and the *phenylhydrazone*, obtained by the action of phenylhydrazine on the ketopyrazolone in acetic acid solution, occurs in orange-red crystals and melts at 170°.

1:3-Diphenyl-4-ketopyrazolone condenses with *o*-phenylenediamine to form a red *substance*, which has the composition $C_{21}H_{16}ON_4$, melts at 240—241°, and by long-continued ebullition of its solution in acetic acid is converted into the normal *azine*, $C_{21}H_{14}N_4$, which crystallises in yellow needles and melts at 231°. With *o*-tolylenediamine, a

similar *azine*, crystallising in long needles, is formed. Hydrazine reacts with the ketopyrazolone to form a cinnabar-red *compound* of the composition $C_{15}H_{12}ON_4$, which melts at 98—101°.

When 1 : 3-diphenyl-4-ketopyrazolone is mixed with phenylhydrazine dissolved in alcohol, there separates a yellow additive *product* of the formula $N{<}\begin{array}{l}CPh{-}C(OH){\cdot}NH{\cdot}NHPh\\ \quad\; | \\ NPh{\cdot}CO\end{array}$, which decomposes slowly at the ordinary temperature and explosively at 82°, forming a *product* which may be either 4-*hydroxy*-1 : 3-*diphenylpyrazolone*, $N{<}\begin{array}{l}CPh{-}CH{\cdot}OH\\ \quad\; | \\ NPh{\cdot}CO\end{array}$, or the isomeric 4 : 5-*dihydroxy*-1 : 3-*diphenylpyrazole*, $N{<}\begin{array}{l}CPh{\cdot}C{\cdot}OH\\ \quad\;\; \| \\ NPh{\cdot}C{\cdot}OH\end{array}$. It crystallises in silver-white leaflets and melts at 200—208°. The *dibenzoyl* derivative forms white needles.

4-*Hydroxy*-1 : 3-*diphenyl*-2-*methylpyrazolone*, $NMe{<}\begin{array}{l}CPh{-}C{\cdot}OH\\ \quad\; | \\ NPh{\cdot}CO\end{array}$, obtained by the action of methyl iodide on diphenylketopyrazolone, forms brilliant needles, melts at 221°, and is soluble in alcohol and chloroform, less so in water and acetone. The *sodium* derivative is sparingly soluble. The *methyl ether* forms white needles melting at 155°, and the *benzoyl* derivative colourless needles melting at 190°.

T. A. H.

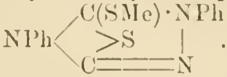
Compounds of Dimethylaminophenyldimethylpyrazolone with Camphoric Acid. Farbenwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 135729).—A solution of 1 mol. of camphoric acid and 1 or 2 mols. of dimethylaminophenyldimethylpyrazolone in dry ether is concentrated in a vacuum in absence of light. The product is sensitive to light, but is stable when preserved in bottles of amber glass. The salts find therapeutic application.

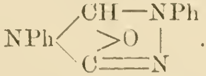
The *dimethylaminophenyldimethylpyrazolone hydrogen camphorate* is crystalline and melts at 94° after washing with light petroleum; the *normal* salt is a fine white powder melting at 81—82°. C. H. D.

Indanthrene. Rene Bohn (*Ber.*, 1903, 36, 1258—1260).—Controversial, in reply to F. Kaufler (this vol., i, 446). T. M. L.

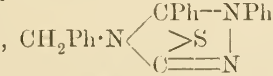
Heterodicyclic Compounds of the Thiodiazole and Triazole Series. Max Busch (*J. pr. Chem.*, 1903, [ii], 67, 201—264. Compare Abstr., 1899, i, 825, 949—957; 1901, i, 234).—The *iso*dithiodiazolones are shown to be best represented by the formula $S{<}\begin{array}{l}CR{-}NR\\ \;\;{>}S\;\; | \\ C{\equiv}N\end{array}$, and are termed by the author *endo*thio-thiodiazolines. The prefix endo- denotes a mobile atom forming a bridge between two atoms in a ring Thus diphenyl*iso*dithiodiazolone (Abstr., 1899, i, 953) becomes (3 : 5)-*endo*thio-1 : 5-diphenylthiodiazoline. The *endo*thio-thiodiazolines are well-characterised substances of high melting point, which are indifferent to acids, but easily decomposed by alkalis. To the *endo*thio-triazole group

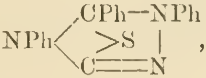
belongs the compound formed by the action of thiocarbonyl chloride on *a*-diphenylthiosemicarbazide methyl ether (Abstr., 1901, i, 236), now termed *endo*thio-1 : 4-diphenyl-5-methylmercaptodihydrotriazole,



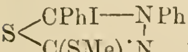
Marckwald's diphenyliminodiazolone (Abstr., 1893, i, 28) is *endo*oxy-1 : 4-diphenyltriazole, 

[With W. Kamphausen and Sebastian Schneider.]—*endo*Thiodiphenylthiodiazoline, in boiling benzene solution, is not attacked by mercuric oxide, but at 100° under pressure it yields a small amount of a substance crystallising in prisms and melting at 178°, probably *s*-dibenzoylhydrazine. In boiling alcoholic solution, the thiodiazoline is decomposed by mercuric oxide. Dilute nitric acid and potassium permanganate oxidise it to benzanilide.

The action of ammonia on *endo*thiodiphenylthiodiazoline leads to the formation of 1-phenylthiosemicarbazide, the action of benzylamine to that of 1-phenyl-4-benzylthiosemicarbazide and endo*thio*-1 : 5-*diphenyl*-4-*benzyldihydrotriazole*, , which crystallises in long, glistening needles, melts at 236°, and is soluble in chloroform, less so in alcohol.

*endo*Thio-1 : 4 : 5-triphenyldihydrotriazole, , is formed by the action of benzaldehyde on *β*-diphenylthiosemicarbazide (Abstr., 1901, i, 235), by the action of aniline on *endo*thiodiphenylthiodiazoline at 150—160°, or by the action of benzoyl chloride on diphenylthiosemicarbazide; it crystallises in colourless needles and melts at 334—336°. endo*Thio*-1 : 5 *diphenyl*-4-p-*tolyldihydrotriazole* crystallises in yellow prisms and melts and decomposes at 301—303°. endo*Thio*-1 : 5-*diphenyl*-4-o-*tolyldihydrotriazole* crystallises in glistening, yellow prisms and melts and decomposes at 249—250°.

In chloroform solution, *endo*thiodiphenylthiodiazoline unites with 2 atoms of iodine forming a *periodide*, $C_{14}H_{10}N_2S_2I_2$, which crystallises in scarlet, glistening crystals and melts at 145°.

The action of methyl iodide on *endo*thiodiphenylthiodiazoline leads to the formation of 5-*iodo*-3-*methylthiol*-1 : 5 *diphenylthiodiazoline*, , which crystallises in clusters of needles, melts and evolves methyl iodide with formation of the *endo*thio-thiodiazoline at 188°, is easily soluble in chloroform or warm alcohol, forms a periodide, $C_{15}H_{13}N_2S_2I,I_2$, which melts at 121°, and is also obtained from 3-methylthioldiphenylthiodiazoline, and when warmed with dilute sodium hydroxide solution yields methylbenzoylphenyldithiocarbazinate. The action of sodium ethoxide on iodomethylthioldiphenylthiodiazoline leads to the formation of *ethoxymethylthioldiphenylthiodiazoline*,

$$\mathrm{S}{<}\begin{matrix}\mathrm{CPh(OEt)}\\ \mathrm{C(SMe){:}N}\end{matrix}{>}\mathrm{NPh},$$

the action of aqueous alkalis, alkali carbonate, or silver oxide and alcohol gives rise to the ethoxy-compound and methyl benzoyldithiocarbazinate. In ethereal solution, the ethoxy-compound is converted by alcoholic hydrogen chloride into *methylthiolchlorodiphenylthiodiazoline*, which crystallises in colourless needles, melts at 120°, and is converted by alcoholic hydriodic acid into the corresponding iodo-compound. The chlorothiodiazoline is converted by aqueous sodium hydrogen carbonate solution into a light yellow, amorphous *powder* which, on treatment with alcohol, yields methyl benzoylphenyldithiocarbazinate. *Methoxymethylthioldiphenylthiodiazoline*, formed by the action of sodium methoxide on the iodide, crystallises in pointed prisms, melts at 82°, and with alcoholic hydrogen chloride yields the chloride melting at 120°. With alcoholic ammonia, the iodide yields methyl benzoylphenyldithiocarbazinate and 3-methylthiol-1 : 5-diphenyltriazole, which melts at 103—104° and is identical with Wheeler and Beardsley's compound (Abstr., 1902, i, 502).

endo*Thio*-1 : 5-*diphenyl*-4-*ethyldihydrotriazole*, $$\mathrm{NEt}{<}\begin{array}{l}\mathrm{CPh{\cdot}NPh}\\ \quad{>}\mathrm{S}\ |\\ \mathrm{C{=\!=}N}\end{array}$$

formed by the action of ethylamine on iodomethylthioldiphenylthiodiazoline, crystallises in glistening rhombohedra, melts at 232°, is easily soluble in chloroform, and is indifferent to acids. The action of benzylamine on the iodothiodiazoline leads to the formation of *endo*thio-diphenylbenzyldihydrotriazole, which combines with methyl iodide forming 5-*iodo*-3-*methylthiol*-1 : 5-*diphenyl*-4-*benzyldihydrotriazole*,

$$\mathrm{CH_2Ph{\cdot}N}{<}\begin{array}{l}\mathrm{CPhI{-\!-}NPh}\\ \mathrm{C(SMe){:}N}\end{array},$$

which crystallises in long leaflets, melts at 176°, and is converted by aqueous potassium hydroxide into 5-*hydroxy*-3-*methylthiol*-1 : 5-*diphenyl*-4-*benzyldihydrotriazole*, which crystallises in slender, colourless, matted needles, melts at 135°, is easily soluble in alcohol, and has basic properties, forming a *chloride* with hydrochloric acid and the iodide with hydriodic acid.

5-*Iodo*-3-*methylthiol*-1 : 3 : 5-*triphenyldihydrotriazole*, formed by the action of aniline on the iodothiodiazoline, by the addition of methyl iodide to *endo*thiotriphenyldihydrotriazole, or by the action of iodine on methylthioltriphenyldihydrotriazole, crystallises in clusters of flat needles, melts at 330°, is easily soluble in chloroform, and is converted by potassium hydroxide and alcohol into *hydroxymethylthioltriphenyldihydrotriazole*, which crystallises in colourless, glistening leaflets or clusters of long prisms and melts at 157°. With alcoholic ammonia, the iododihydrotriazole yields endo*iminotriphenyldihydrotriazole*,

$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{CPh{-\!-}NPh}\\ \quad{>}\mathrm{NH}\ |\\ \mathrm{C{=\!=\!=}N}\end{array},$$

which crystallises in white, silky needles, melts at 203°, and is a weak base; the *hydrochloride* crystallises in needles and melts at

200°. The *endo*imino-compound is also formed by action of alcoholic ammonia on *endo*thiotriphenyltriazole at 210—220°.

The action of hydrazine hydrate on iodomethylmercaptodiphenylthiodiazoline leads to the formation of *diphenyl*-s-N-*dihydrotetrazinethiol*, $CPh\ll\begin{matrix}NPh\cdot N\\N\cdot NH\end{matrix}\gg C\cdot SH$, which crystallises in clusters of small needles, melts at 208°, and dissolves in aqueous sodium carbonate to a yellow solution. The action of phenylhydrazine on the iodothiodiazoline leads to the formation of *methyl benzoylphenyldithiocarbazinate-phenyl hydrazone*, NHPh·N:CPh·NPh·NH·CS·SMe, which crystallises in small, glistening, red needles, melts at 145—146°, is easily soluble in chloroform or benzene, is at once slightly basic and acid, is hydrolysed to the methyl ester by boiling acids, and when fused forms endo*thio-4-anilino*-1 : 5 *diphenyldihydrotriazole*, $NHPh\cdot N\begin{matrix}\diagup CPh\cdot NPh\\ \quad >S\ | \\ \diagdown C\!=\!=\!N\end{matrix}$; this crystallises in small, thick, yellow needles, melts at 132°, is easily oxidised, forms a *hydrochoride*, and with nitrous acid yields a *nitrosoamine*.

Bromomethylthioldiphenylthiodiazoline perbromide, $C_{15}H_{13}N_2S_2Br,Br_2$, resembles the iodide, crystallises in yellow, matted needles, melts at 172°, is insoluble in most solvents, and when boiled with alcohol yields a *dibromomethylthioldiphenylthiodiazoline*, which crystallises in needles and melts at 196°. With dilute sodium hydroxide, it forms a *brominated* methyl benzoylphenyldithiocarbazinate which crystallises in needles, melts at 165°, and is soluble in alkalis. With benzylamine, the bromothiodiazoline forms bromo*endo*thiodiphenylbenzyldihydrotriazole, which crystallises in glistening leaflets and melts at 218°.

[With ALBERT SPITTA.]—The addition of ethyl bromide to *endo*thiodiphenylthiodiazoline takes place with greater difficulty than does the addition of ethyl or methyl iodide.

Bromoethylthioldiphenylthiodiazoline crystallises in colourless prisms, melts and decomposes at 185—187°, and with aqueous potassium iodide solution forms the corresponding iodothiodiazoline.

Ethylthioldiphenylthiodiazoline, formed by the action of benzaldehyde on ethyl phenyldithiocarbazinate, crystallises in yellow needles, melts at 70°, and with bromine in benzene solution yields the *perbromide* of bromoethylthioldiphenylthiodiazoline. The perbromide crystallises in yellow, matted needles, melts at 174°, and when boiled with alcohol forms dibromodiphenylethylthiolthiodiazoline, which crystallises in white, flat needles and melts at 184°. With benzylamine, it forms bromo*endo*thiodiphenylbenzyldihydrotriazole melting at 218°. When dissolved in aqueous sodium hydroxide, the bromide forms ethyl bromobenzoylphenyldithiocarbazinate, which crystallises in colourless needles and melts at 117°.

Iodoethylthioldiphenylthiodiazoline crystallises in glistening, yellow prisms, melts and decomposes at 193—194°, and is fairly soluble in warm alcohol. The *periodide* crystallises in large, glistening, reddish-brown needles and melts at 141°. When boiled with alcohol or dilute alkali, the iodide is converted into ethyl benzoylphenyldithiocarbazinate melting at 164—165°. 3-Ethylthiol-1 : 5-diphenyltriazole (Wheeler

and Beardsley, *loc. cit.*) is formed by the action of ammonia on the iodide.

Iodoethylthioltriphenyldihydrotriazole crystallises in yellow prisms and melts and decomposes at 304°. The corresponding *hydroxy*-compound crystallises in colourless leaflets and melts at 153°. *Iodoethylthioldiphenyl*-4-o-*tolyldihydrotriazole* crystallises in colourless leaflets and melts at 245°. *Iodoethylthioldiphenyl*-4-p-*tolyldihydrotriazole* forms colourless prisms and melts at 256°. *Iodoethylthioldiphenyl*-4-α-*naphthylhydrotriazole* forms yellow, four-sided leaflets and melts at 278°. *Iodoethylthioldiphenyl*-4-β-*naphthyldihydrotriazole* crystallises in yellow needles and melts at 208°.

[With Sebastian Schneider.]—*endo*Thiophenylthiodiazoline (Abstr., 1896, i, 190) is best prepared by the action of formiminoether hydrochloride on potassium phenyldithiocarbazinate. In this compound, the ring is less stable than in the diphenyl derivative; with aniline, it forms β-diphenylthiosemicarbazide and formic acid.

Iodomethylthiolphenylthiodiazoline, $S<\begin{matrix}CHI—NPh\\ C(SMe):N\end{matrix}$, crystallises in thick leaflets and melts at 151°. When warmed with water, aniline, or benzylamine, the iodide is hydrolysed to methyl phenyldithiocarbazinate and formic acid.

endo*Thio*-1 : 4-*diphenyldihydrotriazole,* $NPh<\begin{matrix}CH\cdot NPh\\ >S\ |\\ C{=}N\end{matrix}$, formed by the action of formic acid on β-diphenylthiosemicarbazide, crystallises in small, colourless needles and melts at 214—215°. It is indifferent to acids, but is decomposed with formation of diphenylthiosemicarbazide when warmed with alcohol and a small amount of sodium hydroxide. *Iodomethylthioldiphenyldihydrotriazole* crystallises in colourless, matted needles and melts at 243°.

*endo*Thio-1-phenyl-5-methylthiodiazoline, formed by the action of acetyl chloride on potassium phenyldithiocarbazinate (Abstr., 1896, i, 190), resembles the diphenyl derivative. The action of sodium hydroxide on methylthiolphenylmethylthiodiazoline leads to the formation of *methyl acetylphenyldithiocarbazinate,* which crystallises in glistening needles and melts at 126°. endo*Thio*-1 : 4-*diphenyl*-5-*methyldihydrotriazole* crystallises in short, white needles and melts at 253°.

The action of acetyl chloride on β-diphenylthiosemicarbazide leads to the formation of a *substance,* $C_{15}H_{14}N_3SCl$, which crystallises in glistening leaflets and melts at 218°; when treated with alcoholic ammonia, it yields *endo*thiodiphenylmethyldihydrotriazole, but with aqueous ammonia or alkalis it is converted into a *substance,*

$$C_{23}H_{23}ON_5S,$$

which forms thick crystals and melts at 152°. *Iodomethylthioldiphenylmethyldihydrotriazole* crystallises in colourless needles and melts at 250°.

endo*Thiophenylbenzylmethyldihydrotriazole,* $CH_2Ph\cdot N<\begin{matrix}CMe\cdot NPh\\ >S\ |\\ C{=}N\end{matrix}$, crystallises in silky needles and melts at 205°.

[With E. Blume.]—The action of benzoyl chloride on potassium *p*-tolyldithiocarbazinate leads to the formation of endo*thio*-5-*phenyl*-1-p-

tolylthiodiazoline, which crystallises in glistening, orange-coloured leaflets and melts at 205—206°. With benzylamine, it yields hydrogen sulphide and β-1-*p*-tolyl-4-benzylthiosemicarbazide, which crystallises in delicate, glistening needles and melts at 156°. Dixon's tolylbenzylthiosemicarbazide (Trans., 1892, 61, 1022) is probably the α-form.

endo*Thiodiphenyl*-1-p-*tolyldihydrotriazole* crystallises in yellow needles and melts at 340°. *Phenyliodomethylthiolphenyl*-p-*tolylthiodiazoline* crystallises in glistening, golden leaflets and melts at 188°. When warmed with dilute alkalis and acidified, it yields *methyl benzoyl*-p-*tolyl dithiocarbazinate*, which crystallises in glistening, white needles and melts at 160°, but if warmed with dilute alcoholic alkalis yields the thiodiazoline ether. *Methoxymethylthiolphenyl*-p-*tolylthiodiazoline* crystallises in glistening, white needles and melts at 95°. The *ethoxy*-compound crystallises in glistening, white needles and melts at 83°. endo*Thio-5-phenyl*-1-p-*tolyl*-4-*benzyldihydrotriazole*, formed from benzylamine and the iodide, crystallises in colourless, glistening leaflets or prisms and melts at 234°. With aniline, the iodide forms *iodomethylthiol*-4:5-*diphenyl*-1-p-*tolyldihydrotriazole*, $NPh<\begin{matrix}CPhI-N\cdot C_7H_7\\ C(SMe):N\end{matrix}$, which crystallises in small, white needles, melts at 270°, and, with dilute alkalis, sodium methoxide or ethoxide, yields the *hydroxy*-compound, which crystallises in needles and melts at 136°.

[With Sebastian Schneider.]—1:4-Diphenylsemicarbazide, which melts at 176°, is converted by boiling concentrated formic acid into *formyldiphenylsemicarbazide*, CHO·NPh·NH·CO·NHPh, which crystallises in silvery leaflets and melts at 170°. Dilute formic acid converts diphenylsemicarbazide into formylphenylhydrazine. *endo*Oxy-1:4-diphenyldihydrotriazole, $NPh\begin{matrix}\diagup CH-NPh\\ >O\ \ |\\ \diagdown C{=\!=}N\end{matrix}$, which is obtained by heating formyldiphenylsemicarbazide at 180°, melts at 256°, and is identical with Marckwald's diphenyliminodiazolone (*loc. cit.*). The *endo*oxytriazole does not form an additive product with methyl iodide. Boiling alcoholic potassium hydroxide hydrolyses it to diphenylsemicarbazide.

G. Y.

Synthesis of Hydroxyphenyltriazoles and [its bearing on] Spatial Hindrance. Hans Rupe and Gustav Metz (*Ber.*, 1903, 36, 1092—1104).—Rupe and Labhardt have shown (Abstr., 1900, i, 258) that carbamic chloride and β-acylphenylhydrazines interact to form hydroxyphenyltriazoles. When, however, in the molecule

NHPh·NH·CO·R,

R = Ph, it was noted that there was no action at all with carbamic chloride. This was attributed to spatial hindrance, a view which received support from the fact that when R = CH_2Ph, interaction with carbamic chloride took place.

The authors find that when R = a completely reduced benzene ring, triazoles are readily formed. That no triazole formation occurs

when $R = Ph$ is therefore due to the negative unsaturated character of benzene. This conception of the influence of negative unsaturated groups is further borne out by experiments with *n*-butyryl-, crotonyl-, hydrocinnamoyl-, and cinnamoyl-phenylhydrazines.

β-Hexahydrobenzoylphenylhydrazine, $NHPh\cdot NH\cdot CO\cdot C_6H_{11}$, prepared from phenylhydrazine and hexahydrobenzoyl chloride, crystallises from alcohol in beautiful, white prisms melting at 164°. When dissolved in benzene and then treated with carbamic chloride, it yields 1-*phenyl-3-hexahydrophenyl-5-triazolone-3-carboxylamide*,

$$\begin{matrix} N{:}C(C_6H_{11}) \\ NPh\text{——}CO \end{matrix}\!\!>\!N\cdot CO\cdot NH_2,$$

which crystallises from anhydrous acetone in long, white needles, melts above 300°, and is easily soluble in warm alcohol, acetone, and ethyl acetate, but sparingly so in benzene. When the crude product is twice crystallised from absolute alcohol, 5-*hydroxy*-1-*phenyl*-3-*hexahydrophenyltriazole*, $\begin{matrix} N{=}C(C_6H_{11}) \\ NPh\cdot C(OH) \end{matrix}\!\!\geqslant\!N$, is obtained. It may also be prepared by dissolving the crude product in sodium hydroxide solution and then adding mineral acid. It crystallises from ethyl acetate in white, stellar, tiny needles melting at 196—197°. Its *acetyl* derivative forms long, white, asbestos-like needles and melts at 107—108°; the acetyl group is eliminated by boiling with water, but less readily than is generally the case with substances of this type.

1-*Phenyl-3-propyl-5-triazolone-4-carboxylamide*,

$$\begin{matrix} N{=}CPr^{\alpha} \\ NPh\cdot CO \end{matrix}\!\!>\!N\cdot CO\cdot NH_2,$$

prepared by boiling *n*-butyrylphenylhydrazine (m. p. 103—104°) with carbamic chloride in benzene solution, crystallises from dry benzene in white needles or prisms melting at 133°. When the crude product is crystallised from aqueous alcohol, 5-*hydroxy*-1-*phenyl*-3-*propyltriazole* is formed, but is best obtained from the original material by dissolving in sodium hydroxide and adding a mineral acid. It crystallises from ethyl acetate in long, white needles and melts at 146°. Its *acetyl* derivative crystallises from alcohol in brilliant, flat prisms and melts at 84°.

β-Crotonylphenylhydrazine, $NHPh\cdot NH\cdot CO\cdot CH{:}CHMe$, crystallises from ethyl acetate in brilliant, small leaflets or scales and melts at 190°. It yields 5-*hydroxy*-1-*phenyl*-3-*propenyltriazole*,

$$OH\cdot C_2N_3Ph\cdot CH{:}CHMe,$$

which forms brilliant, faintly yellow, small needles, melts at 188°, and when dissolved in chloroform and treated with bromine yields 5-*hydroxy*-1-*phenyl*-3-*αβ-dibromopropyltriazole*,

$$OH\cdot C_2N_3Ph\cdot CHBr\cdot CHMeBr,$$

as glittering, faintly yellow, microscopic prisms melting at 128°.

5-*Hydroxy*-1-*phenyltriazole-3-carboxylic acid*, $OH\cdot C_2N_3Ph\cdot CO_2H$, prepared by oxidising 5-hydroxy-1-phenyl-3-propenyltriazole with alkaline potassium permanganate, melts at 179—180°.

β-Hydrocinnamoylphenylhydrazine, $NHPh\cdot NH\cdot CO\cdot CH_2\cdot CH_2Ph$, crystallises from dilute alcohol in white needles and melts at 116—117°. The crude product, obtained by treatment with carbamic chloride, did

not, in this case, yield an amide when crystallised from boiling alcohol. The hydroxytriazole, $OH\cdot C_2N_3Ph\cdot CH_2\cdot CH_2Ph$, crystallises from dilute alcohol in very small, faintly yellow needles, melting at 182—183°. Its *acetyl* derivative melts at 109°.

When carbamic chloride was treated with β-cinnamoylphenylhydrazine, no hydroxytriazole was obtained. A. McK.

Hydroxyphenyltriazoles. HANS RUPE and HANS LABHARDT (*Ber.*, 1903, **36**, 1104—1105).—Acree (Abstr., 1902, i, 212) considers Pinner's phenylurazole to be 3-hydroxy-1-phenyl-5-triazole. He obtained it from a substance which he regarded as ethyl diphenylsemicarbazidedicarboxylate, but the authors, who have previously prepared the same substance by the same method, found it to be the carbamide of ethyl phenylhydrazidoformate [ethyl phenylsemicarbazide-α carboxylate] (Abstr., 1899, i, 356).

In the amides formed by the primary action of carbamic chloride on β-acylphenylhydrazines, the group $CO\cdot NH_2$ is attached to N, whilst in the acetyl derivatives of the hydroxytriazoles the acetyl group is very probably attached to oxygen. In the strongly acid triazole compounds, the nitrogen derivatives are often quite as labile as the oxygen derivatives. A. McK.

2 : 4-Dialkylsemicarbazides and their Intramolecular Transformations. MAX BUSCH and ROBERT FREY (*Ber.*, 1903, **36**, 1362—1379).—Phenylcarbimide reacts with an absolute ethereal solution of formazyl hydride (Abstr., 1893, i, 83) yielding carbanilinoformazyl hydride, $NHPh\cdot CO\cdot NPh\cdot N\colon CH\cdot N\colon NPh$. This crystallises from benzene or alcohol in yellowish-red needles, melts and decomposes at 178°, and has feebly acidic properties. When hydrolysed with 20 per cent. sulphuric acid and alcohol, it yields 2 : 4-diphenylsemicarbazide (compare preceding abstract). The same compound is obtained when 1-acetyl-2 : 4 diphenylsemicarbazide (Freund and König, Abstr., 1894, i, 96; Vahle, *ibid.*, 411) is hydrolysed in a similar manner, or when the 2 : 4-*diphenylsemicarbazone* of *methyl dithiocarbonate* is hydrolysed. The latter, $NHPh\cdot CO\cdot NPh\cdot N\colon C(SMe)_2$, is obtained by the methylation of the 2 : 4-diphenylsemicarbazide of methyl 1-dithiocarbazinate (Abstr., 1901, i, 234). It crystallises from alcohol, melts at 105°, and dissolves in the usual solvents.

The *hydrochloride* of 2 : 4-diphenylsemicarbazide forms colourless needles, melts and decomposes at 186°, and is decomposed by water. The *platinichloride* crystallises in yellow needles. On treatment with nitrous acid, the semicarbazide yields *s*-diphenylcarbamide; with benzaldehyde, it yields benzaldehyde-2 : 4-diphenylsemicarbazone, and with phosgene, 2 : 4-diphenylurazole (Abstr., 1901, i, 617). With phenylcarbimide, it forms 1-*carbanilino*-1 : 4-*diphenylthiosemicarbazide*, $NHPh\cdot CO\cdot NPh\cdot NH\cdot CS\cdot NHPh$, crystallising in colourless needles and melting at 170°; the *hydrochloride* melts at 190°.

2 : 4-Diphenylsemicarbazide is completely transformed into the 1 : 4-isomeride (m. p. 176°) when heated for half an hour at 170—175°. It is not oxidised by ferric chloride and does not give Bülow's reaction. Vahle's 1-acetyl-1 : 4-diphenylsemicarbazide (*loc. cit.*) melts at 192° and

not at 183°, and the isomeric 1-acetyl-2 : 4-derivative at 184° and not at 175—178°.

Methyl *o*-tolyldithiocarbazinate melts at 148° and reacts with phenylcarbimide, yielding *methyl* 2-o-*tolyl*-4-*phenylsemicarbazide*-1-*dithiocarboxylate*, $NHPh\cdot CO\cdot N(C_7H_7)\cdot NH\cdot CS\cdot SMe$, which crystallises in colourless needles, sparingly soluble in alcohol or ether. When methylated at the ordinary temperature in the presence of alcohol and alkali, it yields the o-*tolylphenylsemicarbazone* of *methyl dithiocarbonate*,

$$NHPh\cdot CO\cdot N(C_7H_7)\cdot N(SMe)_2,$$

in the form of colourless needles melting at 98°. When this is hydrolysed, 4-*phenyl*-2-o-*tolylsemicarbazide* is obtained in the form of compact, colourless needles or prisms melting at 136°. With benzaldehyde, it yields a *semicarbazone* melting at 118°, and when heated at 175° for some time is partially transformed into the isomeric 4-*phenyl*-1-o-*tolylsemicarbazide*, which may also be obtained by the union of *o*-tolylhydrazine and phenylcarbimide. It crystallises in glistening needles, melts at 142°, is readily soluble in most solvents, and with nitrous acid yields a *nitrosoamine* which turns red at about 70° and melts at 116°. *o-Tolylazocarbanilide*, $C_7H_7N{:}N\cdot CO\cdot NHPh$, obtained by the oxidation of the 1 : 4-*o*-tolylphenylsemicarbazide with ferric chloride, forms dark red needles which melt and decompose at 132—133°.

Methyl m-*tolyldithiocarbazinate* crystallises in colourless needles or plates and melts at 111°. *Methyl* m-*tolylphenylsemicarbazidedithiocarboxylate* melts at 152° and the m-*tolylphenylsemicarbazone* of *methyl dithiocarbonate* at 127°. On hydrolysis, the latter yields 4-*phenyl*-2-m-*tolylsemicarbazide* in the form of colourless needles melting at 112° and readily transformed at 160° into the isomeric 4-*phenyl*-1-m-*tolylsemicarbazide* melting at 159°.

Di-*p*-tolylformazyl, $C_7H_7\cdot NH\cdot N{:}CH\cdot N{:}N\cdot C_7H_7$, crystallises in reddish-brown needles melting and decomposing at 105°. With phenylcarbimide, it yields the *carbanilino*-compound,

$$NHPh\cdot CO\cdot N(C_7H_7)\cdot N{:}CH\cdot N{:}N\cdot C_7H_7,$$

melting and decomposing at 184—185°. When this latter is hydrolysed, 4-*phenyl*-2-p-*tolylsemicarbazide* is obtained in the form of colourless plates melting at 184—185°. It dissolves readily in organic solvents and is basic in character. The *hydrochloride* crystallises in colourless needles, melts and decomposes at 170°, and is decomposed by water. With nitrous acid, it yields phenyl-*p*-tolylcarbamide. With benzaldehyde, the semicarbazide yields *benzaldehyde*-4-*phenyl*-2-*tolylsemicarbazone*, $NHPh\cdot CO\cdot N(C_7H_7)\cdot N{:}CHPh$, in the form of colourless needles melting at 176—177°. 4-*Phenyl*-1-p-*tolylsemicarbazide*, obtained from *p*-tolylhydrazine and phenylcarbimide or by intramolecular transformation of the 2 : 4-compound at 176—177°, crystallises from alcohol in large, glistening needles and melts at 171°. When oxidised, it yields p-*tolylazocarbanilide* in the form of light yellow needles melting and decomposing at 129°.

Methyl 2-*phenyl*-4-*ethylsemicarbazide*-1-*dithiocarbazinate*,

$$NHEt\cdot CO\cdot NPh\cdot NH\cdot CS\cdot SMe,$$

obtained from ethylcarbimide and methyl phenyldithiocarbazinate, crystallises in colourless prisms which soften at 120° and melt at 122°.

When methylated, it yields the *phenylethylsemicarbazone* of methyl dithiocarbonate, $NHEt{\cdot}CO{\cdot}NPh{\cdot}N{:}C(SMe)_2$, melting at 106° and readily soluble in most solvents. This, on hydrolysis, gives 4-*ethyl*-2-*phenylsemicarbazide*, which crystallises from dilute alcohol in colourless plates melting at 88°, and is soluble in all solvents including water. With *m*-nitrobenzaldehyde, it yields a *phenylethylsemicarbazone*,

$$NHEt{\cdot}CO{\cdot}N{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2,$$

melting at 153°. When heated at 165—170°, the 2-phenyl-4-ethylsemicarbazide is partially transformed into the 1-phenyl-4-ethyl compound melting at 151° (Fischer, *Annalen*, 1878, **190**, 109).

Acetylphenylethylsemicarbazide crystallises in small needles, melts at 92°, and when hydrolysed with dilute sulphuric acid yields phenylhydrazine. *o*-Nitrophenyldiazonium chloride reacts with malonic acid yielding the o-*nitrophenylhydrazone* of *glyoxylic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CH{\cdot}CO_2H,$$

melting at 202°, and not a formazyl derivative. J. J. S.

m-**Azophenol.** Karl Elbs and W. Kirsch (*J. pr. Chem.*, 1903, [ii], **67**, 265—273. Compare Abstr., 1899, i, 270).—m-*Azophenol*, formed by diazotisation of *m*-diaminoazobenzene, crystallises in light yellow, glistening leaflets, melts at 205°, is easily soluble in hot alcohol, ether, acetone, or glacial acetic acid, and dissolves in very dilute aqueous sodium hydroxide to a red, in aqueous ammonia or cold sodium carbonate to a brownish-yellow, solution. The *diacetyl* derivative crystallises in yellow needles, melts at 137°, and is easily soluble in hot alcohol, benzene, acetone, or glacial acetic acid, but insoluble in water or aqueous sodium hydroxide. The *dibenzoyl* derivative crystallises in yellowish-brown needles and melts at 129°. p-*Nitro*-m-*azophenol*, $OH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}NO_2$, formed by nitrating azophenol in cold glacial acid solution, crystallises in yellowish-brown needles, melts at 205°, and is easily soluble in hot dilute alcohol, ether, or glacial acetic acid, and forms a yellowish-brown *sodium* derivative which is easily soluble in water. *Diacetyl*-p-*nitro*-m-*azophenol*, formed by acetylating nitroazophenol or by nitrating diacetylazophenol, crystallises in brownish-yellow leaflets, melts at 141°, and is easily soluble in ether, acetone, or glacial acetic acid. When boiled with water and zinc dust, *m*-azophenol forms a colourless solution, which probably contains m-*hydrazophenol*, as the solution becomes red and deposits azophenol when shaken with air. If the colourless solution is poured, when boiling, into fuming nitric acid, *m*-dihydroxybenzidine crystallises out on cooling. *Tetra-acetyl*-2 : 2′-*dihydroxybenzidine*, $C_{12}H_8(OAc)_2(NHAc)_2$, crystallises in colourless leaflets, melts at 128°, and is easily soluble in hot alcohol. When diazotised and coupled with R-salt, 2 : 2′-dihydroxybenzidine forms a dye, which is precipitated by dilute hydrochloric acid as a dark brownish-red powder, dissolves in water to a red solution, and dyes cotton wool bluish-violet in an alkaline bath; on addition of hydrochloric acid, the colour changes to a pure blue.

Reduction and treatment with acid of *p*-nitro-*m*-azophenol leads to the formation of 5-*amino*-2 : 2′-*dihydroxybenzidine hydrochloride*, $OH{\cdot}C_6H_3(NH_2){\cdot}C_6H_2(NH_2)_2{\cdot}OH,2HCl$, which remains unchanged at 340° and is easily soluble in water and reprecipitated on addition of

concentrated hydrochloric acid. The aqueous solution of the salt gradually becomes coloured brown; when diazotised and coupled with R-salt, aminodihydroxybenzidine yields a red solution which dyes cotton wool a pure blue. G. Y.

Action of *p*-Nitrobenzaldehyde on Ethyl Phenylazoaceto-acetate. BERNHARD PRAGER (*Ber.*, 1903, 36, 1449—1451).—Whilst *p*-nitrobenzaldehyde readily condenses with ethyl phenylazomethyl-aminocrotonate, $NMe:CMe\cdot CH(N:NPh)\cdot CO_2Et$, to form an additive product, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot C(:NMe)\cdot CH(N:NPh)\cdot CO_2Et$, which is readily hydrolysed to the compound

$$NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot CO\cdot CH(N:NPh)\cdot CO_2Et,$$

the latter cannot be prepared from *p*-nitrobenzaldehyde and ethyl phenylazoacetoacetate. The condensation of these substances only takes place in presence of alkali hydroxides, and then yields the *sodium* derivative of the unsaturated compound

$$NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH(N:NPh)\cdot CO_2Et,$$

which separates from alcohol in yellow needles; the free ester is a yellow powder which darkens above 100° and intumesces at 155°.

By acids, it is hydrolysed to *phenylazo*-p-*nitrobenzylideneacetone*, $NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH_2\cdot N:NPh$, which crystallises from much xylene in orange-coloured, felted needles, darkens at 195°, and melts with intumescence at 210°. T. M. L.

Fatty Aromatic Aminoazo-compounds. III. BERNHARD PRAGER (*Ber.*, 1903, 36, 1451—1459. Compare Abstr., 1902, 64, 578).—The compound, $C_{22}H_{29}ON_5$, prepared by the interaction of diazobenzene and ethyl diethylaminocrotonate is decomposed by alcoholic sulphuric acid yielding alcohol, phenylhydrazine, and a colourless *base*, $C_{14}H_{19}O_2N_3$, which crystallises from light petroleum in obliquely truncated prisms and melts at 66·5—67°; its *picrate* forms yellow, prismatic crystals and melts at 192° (corr.). The formula $NPh:N\cdot C\!\!<\!\!\begin{array}{l}CMe(NEt_2)\cdot NH\\ C(OEt)\text{——}NPh\end{array}$, formerly assigned to the compound $C_{22}H_{29}ON_5$, is now established, and the new base is shown to have the constitution $CO\!\!<\!\!\begin{array}{l}CMe(NEt_2)\cdot NH\\ CO\text{————}NPh\end{array}$; the crystals of the base are colourless but have a blue shimmer, and the solutions in organic media, and especially in benzene, show a blue fluorescence. The same base is produced together with aniline and ammonia when the compound $C_{22}H_{29}ON_5$ is reduced with zinc dust in hydrochloric acid solution.

Alcoholic sodium hydroxide converts the base $C_{14}H_{19}O_2N_3$ into an acid, $C_{14}H_{21}O_3N_3$, which is formulated as

$$NHPh\cdot NH\cdot CMe(NEt_2)\cdot CO\cdot CO_2H,$$

and was isolated in the form of an aurichloride. By the action of dry hydrogen chloride or its alcoholic solution, it is reconverted into the original base with loss of $1H_2O$, and not into an ester; it yields aniline when reduced with zinc dust and hydrochloric acid. T. M. L.

Ethyl Phenylhydrazonecyanoacetate and Phenylazocyanoacetate. Hans Weissbach (*J. pr. Chem.*, 1903, [ii], 67, 395—413. Compare Abstr., 1898, i, 366, and Kjellin, Abstr., 1897, i, 616).—Ethyl α-phenylazocyanoacetate (m. p. 84°) is best prepared by the action of *iso*diazobenzene hydroxide on ethyl cyanoacetate in alcoholic solution below 0°. The product always contains ethyl-α-phenylhydrazonecyanoacetate, which is removed by acetylation. The acetylhydrazone is insoluble, but the unchanged azo-compound is easily soluble in light petroleum. The azo-compound is soluble in aqueous sodium hydroxide, and is reprecipitated unchanged by carbon dioxide, but on addition of hydrochloric acid to the alkaline solution ethyl β-phenylazocyanoacetate is precipitated. The β-form is red, melts at 118°, remains unchanged after repeated fusions or crystallisation from light petroleum. It is not acted on by acetyl chloride. The α- and β-azo-compounds are stereoisomerides.

The action of benzenediazonium chloride on cyanoacetic acid in aqueous solution leads to the formation of formazyl cyanide (Rothenburg, Abstr., 1894, i, 273; Wedekind, Abstr., 1898, i, 193). The hydrolysis of formazyl cyanide by potassium hydroxide leads to the formation of *formazylcarboxylic acid*, $NHPh\cdot N\colon C(CO_2H)\cdot N\colon NPh$, which separates from alcohol in red crystals and melts at 163°. The *silver* salt is a dark violet, the *lead* salt a flesh-coloured precipitate. The anilide could not be prepared from ethyl phenylhydrazonecyanoacetate. The action of carbonyl chloride on the potassium compound of the β-ester leads to the formation of the α-modification.

When heated with acetyl chloride at 90—100° under pressure, ethyl phenylhydrazonecyanoacetate (α or β) forms an unstable *α-acetyl* derivative, which crystallises in white needles, melts at 158°, and on crystallisation from acetone is converted into the *β-acetyl* derivative, which crystallises in plates and melts at 166°.

Hydrolysis of the acetylated ester leads to the formation of *acetylphenylhydrazonecyanoacetic acid*, $NPhAc\cdot N\colon C(CN)\cdot CO_2H$, which crystallises in slender needles, melts at 210°, and yields coloured metallic salts. Hydrolysis of the acetylated ester with an excess of alkali leads to the formation of a *substance* which crystallises in brown needles and melts at 130°.

The action of ammonia on the α- or β-acetyl ester leads to the formation of *acetylphenylhydrazonecyanoacetamide*, which crystallises in golden leaflets and melts at 224° (compare Krückeberg, Abstr., 1894, i, 369).

Ethyl p-tolylhydrazonecyanoacetate yields an *acetyl* derivative, which was obtained in two modifications. The unstable modification crystallises in needles and melts at 216°; the stable modification crystallises in leaflets and melts at 218—219°. The corresponding *acid*, obtained by hydrolysis of the ester, crystallises in slender, yellow needles and melts at 225°. With alcoholic ammonia, the ester forms the corresponding *amide*, which melts at 250°. The action of acetyl chloride at 100° on ethyl *o*-tolylhydrazonecyanoacetate leads to the formation of the stable or β-modification, which melts at 134° and is converted into the α-form by solution in aqueous sodium hydroxide and precipitation by hydrochloric acid. The α-form melts

at 85° and changes into the β- at 100°. Ethyl *m*-xylylhydrazonecyanoacetate gives similar results with acetyl chloride. The β-modification melts at 166°.

Ethyl *p*-tolyl-, *o*-tolyl-, and *m*-xylyl-hydrazonecyanoacetates, when boiled with potassium hydroxide (2 mols.) in aqueous solution, yield respectively p-*tolylhydrazoneacetamide*, which melts at 168°, o-*tolylhydrazoneacetamide*, which melts at 186°, and m-*xylylhydrazoneacetamide*, which melts at 184°. The three substances crystallise in glistening, yellow leaflets. The *p*-tolyl compound forms a *hydrochloride*. The action of nitrous acid on *o*-tolyl- and *m*-xylyl-hydrazoneacetamides leads to the formation of the corresponding nitroso-compounds. *p*-Tolyl- and phenyl-hydrazoneacetamides are decomposed by nitrous acid.

G. Y.

Interaction of Diazonium Salts with Derivatives of Santonin. EDGAR WEDEKIND and O. SCHMIDT (*Ber.*, 1903, **36**, 1386—1394).—The disbenzeneazosantonic acid, previously obtained (Abstr., 1898, i, 596), has probably the structure

$$\begin{array}{l} \qquad\qquad CO\text{———}CH_2\cdot CH\cdot CMe\cdot CH\cdot N{:}NPh \\ CO_2H\cdot CHMe\cdot C(N{:}NPh)\cdot CH_2\cdot CH\cdot CMe\cdot CO \end{array} \quad \text{or}$$

$$\begin{array}{l} \qquad\qquad CO\cdot CH(N{:}NPh)\cdot CH\cdot CMe\cdot CH_2 \\ CO_2H\cdot CHMe\cdot C(N{:}NPh)\cdot CH_2\cdot CH\cdot CMe\cdot CO \end{array} .$$

It is now shown that desmotroposantonin and the santonous acids also combine with diazonium chlorides giving *benzeneazodesmotroposantonins*,

$$CO{<}\begin{array}{l} O\text{———}CH\cdot CH_2\cdot C\cdot CMe{:}C\cdot N{:}NR \\ CHMe\cdot CH\cdot CH_2\cdot C\cdot CMe{:}C\cdot OH \end{array} ,$$

and *benzeneazosantonous acids*,

$$\begin{array}{l} \qquad\qquad\qquad CH_2\cdot CH_2\cdot C\cdot CMe{:}C\cdot N{:}NR \\ CO_2H\cdot CHMe\cdot CH\cdot CH_2\cdot C\cdot CMe{:}C\cdot OH \end{array} .$$

Benzeneazodesmotroposantonin (*benzeneazodimethylhydroxytetrahydronaphtholpropionolactone*), obtained from desmotroposantonin and benzenediazonium chloride, crystallises from benzene in long, felted, yellow needles and melts at 260°. The analogous *compound* from *p*-toluenediazonium chloride separates from alcohol in bright red crystals and melts at 275°; that from *o*-nitrobenzenediazonium chloride crystallises from boiling benzene in dark red needles melting at 275°, and the *compound* from diazotised *p*-aminobenzoic acid decomposes at 260°; the *derivative* obtained from diazotised sulphanilic acid melts at 269°.

Benzeneazodesmotroposantonous acid (*benzeneazodimethyltetrahydronaphtholpropionic acid*), prepared from desmotroposantonous acid and benzenediazonium chloride, crystallises from alcohol in lustrous, red leaflets, and melts and decomposes at 218°; the p-*toluene* compound is similar and melts at 214°. *Benzeneazo*-d-*santonous acid* crystallises in thick, red prisms and melts at 250°; p-*nitrobenzeneazo*-d-*santonous acid* forms bright red leaflets and melts at 175°, and o-*tolueneazodesmotroposantonine* sinters at 285° and melts at 290°. W. A. D.

Azosantonic Acids. EDGAR WEDEKIND (*Ber.*, 1903, **36**, 1395—1397. Compare preceding abstract, and Abstr., 1898, i, 596).—Disbenzeneazosantonic acid, on reduction with stannous chloride and

hydrochloric acid, gives a red *substance*, $C_{42}H_{52}O_8N_6SnCl_6$, which is apparently the *tin* salt of the *aminoazo*-compound,

$$NH_2\cdot C_{15}H_{18}O_4\cdot N_2Ph.$$

The action of *o*-ditolyltetrazonium chloride on santonic acid is not analogous to that of benzenediazonium salts, as it fails to give a compound containing two azo-groups in the molecule of santonic acid; the product is *di-o-tolyldisazodisantonic acid*, $C_{12}H_6Me_2(N_2\cdot C_{15}H_{18}O_4)_2$, which after purification melts at 164—166°.

All attempts to bring about direct combination of santoninic acid with diazonium salts were unsuccessful. W. A. D.

Soluble Arsenates of Albumoses and Gelatoses. KNOLL & Co. (D.R.-P. 135306, 135307, and 135308).—Albumoses, dissolved in water or suspended in alcohol, are mixed with a strong solution of arsenic acid, concentrated under reduced pressure, and after cooling poured into strong alcohol. The yellowish-white products are readily soluble in water and contain 5—8 per cent. of arsenic, according to the nature of the albumose employed.

Gelatin may also be heated directly with arsenic acid, in which case peptonisation first occurs under the influence of the acid. C. H. D.

Crystallisation of Hæmoglobin. EDWARD T. REICHERT (*Amer. J. Physiol.*, 1903, **9**, 97—99).—Crystals of oxyhæmoglobin can be more readily obtained from oxalated blood than from ordinary blood. The best laking agent is ethyl ether, or, better still, ethyl acetate. Asphyxial blood yields crystals more readily than normal blood. In a mixture of bloods, the process of crystallisation is usually retarded, and if the crystalline forms are different, one usually begins to separate before the other. If a mixture of the blood of rat and guinea pig is used, crystals of different form from either blood separately are obtained. W. D. H.

Combination crystals similar to those referred to in the last sentence were described by Halliburton (*Quart. J. Min. Sci.*, 1887) some years ago.—W. D. H.

Specific Rotation of the Nucleic Acid of the Wheat Embryo. THOMAS B. OSBORNE (*Amer. J. Physiol.*, 1903, **9**, 69—71).—Nucleic acid from the wheat embryo is strongly dextrorotatory ($[\alpha]_D$ +67—73·5°), and the degree of rotation is influenced by the concentration of the solution. In mixtures of albumin and nucleic acid, the dextrorotatory action is lessened by the opposite activity of the albumin. In nucleo-proteids, increase in the amount of nucleic acid in combination increases the dextrorotation. W. D. H.

Compounds of Nucleic Acid and its Derivatives with Formaldehyde. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 139907).—Nucleic acid and its derivatives containing phosphorus, such as nucleothymic acid, combine directly with formaldehyde, the products being yellow powders, which are stable in the air and form soluble alkali salts, the solutions of which are stable in the cold, but evolve formaldehyde on heating. C. H. D.

Distinction of two kinds of Catalase. Oskar Loew (*Centr. Bakt. Par.*, 1903, ii, **10**, 177—179).—Experiments made to ascertain whether soluble catalase is mechanically fixed, as supposed by Pozzi-Escot (*Bul. Soc. chim.*, 1902, **27**, 284), gave negative results. The opinion that an insoluble, as well as a soluble, form of catalase exists is therefore adhered to (compare Abstr., 1901, i, 435).

N. H. J. M.

Emulsin, as obtained from Almonds, is a mixture of Several Ferments. Émile Bourquelot and Henri Hérissey (*Compt. rend. Soc. Biol.*, 1903, **55**, 219—221. Compare Abstr., 1902, i, 634, and 744; also *J. Pharm. Chim.*, 1895, [vi], **2**, 327, 376, and 435; and 1902, [vi], **16**, 417).—The product, known as emulsin, contains, besides (1) emulsin, (2) a lactase, (3) probably a gentiobiase, and (4) frequently invertin. N. H. J. M.

Antiferments. Émile Bourquelot and Henri Hérissey (*Compt. rend. Soc. Biol.*, 1903, **55**, 176—178).—Antiferments arrest the action of, but do not destroy, the soluble ferments. There are, however, definite chemical substances which produce similar effects, of which the action of one, namely, lime water, on invertin is described. It is further stated that this action of lime water is destroyed by boiling.

W. D. H.

Action of Mixed Organo-magnesium Compounds on Substances containing Nitrogen. Louis Meunier (*Compt. rend.*, 1903, **136**, 758—759).—The mixed organo-magnesium compounds described by Grignard (Abstr., 1901, i, 263) react with amino- and imino-compounds thus: $NHR_2 + EtMgI = NR_2 \cdot MgI + C_2H_6$. Dry ammonia is rapidly absorbed by an ethereal solution of magnesium ethiodide, a white deposit of amino-magnesium iodide being formed and ethane evolved. When ethereal solutions of aniline and magnesium ethiodide are mixed, a violent reaction takes place, a white precipitate appears, which subsequently redissolves, and ethane is evolved; on evaporating the ether, a *compound*, $NHPh \cdot MgI$, crystallises in pale yellow needles, which are immediately decomposed by water and alcohol. Methylaniline reacts in the same manner with magnesium ethiodide, but dimethylaniline is without action. Diazoaminobenzene and magnesium ethiodide yield ethane and a *compound*, $NPh:N \cdot NPh \cdot MgI$, forming yellowish-brown crystals, which is decomposed by water and alcohol. Phenylhydrazine and magnesium ethobromide yield a *compound*, $MgBr \cdot NPh \cdot NH \cdot MgBr$, which is insoluble in ether. These compounds can all be prepared by treating the amino-derivative with ethyl iodide in ethereal solution in the presence of magnesium powder. K. J. P. O.

Organic Chemistry.

Critical Constants of some Organic Substances. G. B. Vespignani (*Gazzetta*, 1903, 33, i, 73—78).—The author has used the method given by Altschul (Abstr., 1893, ii, 446) for determining the critical constants of some organic substances for which concordant values have not been obtained previously; the following table contains his results:

	Boiling point.	Sp. gr. at 21°/4°.	Critical temp.	Critical pressure (atmospheres).	Critical coefficient. Found.	Critical coefficient. Calc.
Methyl sulphide	38° (760 mm.)	0·8458	231·29°	56·14	8·98	10·75
Ethyl ,, ...	92 (758·5 ,,)	0·8364	284·60	47·1	11·83	15·53
Methyl ethyl sulphide	66 (760 ,,)	0·8369	259·66	41·9	12·71	13·01
Ethyl hydrogen ,,	37 (759·2 ,,)	0·8380	228·3	63·5	7·89	10·85
Acetic anhydride	136·5 (760·6 ,,)	1·0757	296	46·2	12·31	12·69
Propionitrile	98 (760 ,,)	0·7831	258·09	53·8	9·87	8·36
n-Amylene	37·5 (761·5 ,,)	0·6360	202·6	40·4	11·77	12·40
Propionic acid	140·7 (759·8 ,,)	0·9958	339	52·9	11·55	11·01
Ethylene dibromide ...	131 (757·13 ,,)	2·1873	309·83	70·6	8·24	14·50
Carbon tetrachloride...	76·4 (760 ,,)	1·5817	259·5	39·5	13·48	14·35

T. H. P.

Action of Acetylene on Cæsium-Ammonium and on Rubidium-Ammonium. Preparation and Properties of the Acetylene Acetylides, C_2Cs_2,C_2H_2 and C_2Rb_2,C_2H_2, and of the Carbides of Cæsium and Rubidium. Henri Moissan (*Compt. rend.*, 1903, 136, 1217—1222. Compare Abstr., 1899, i, 241).—When acetylene is passed into a solution of cæsium-ammonium in liquid ammonia, the blue colour disappears and ethylene is formed ($3C_2H_2 + 2NH_3Cs = C_2Cs_2,C_2H_2 + 2NH_3 + C_2H_4$). On evaporating the ammonia, transparent crystals of *cæsium acetylide acetylene* are left. This compound is an active reducing agent and very easily enters into reaction with various gases. It melts without decomposition at about 300°, and is violently decomposed by water, giving cæsium hydroxide and acetylene.

Rubidium acetylide acetylene, C_2Rb_2,C_2H_2, is formed in the same way as the cæsium compound and behaves similarly. It forms transparent, hygroscopic crystals, which melt at about 300° with slight decomposition.

Neither of these compounds combines with ammonia as the corresponding calcium one does. When the cæsium compound is heated in a vacuum, it begins to dissociate at about 50° and melts at about 300°. At a slightly higher temperature, decomposition sets in, and

a mixture of acetylene and hydrogen is evolved. The residue consists of *cæsium carbide*, C_2Cs_2, in the form of transparent leaflets. This carbide is readily acted on by fluorine, chlorine, bromine, and iodine, and when warmed with boron or silicon an energetic action takes place. It is decomposed by water, and when heated to dull redness, it decomposes into metal and carbon. *Rubidium carbide*, C_2Rb_2, is formed in the same way and behaves similarly. If rubidium carbide is mixed with an excess of small crystals of calcium and heated in a vacuum, metallic rubidium is volatilised, and deposits on the cold part of the tube in the form of a brilliant mirror which does not attack glass. J. McC.

Electrolytic Preparation of Alcohols, Aldehydes, and Ketones. Martin Moest (D.R.-P. 138442. Compare Abstr., 1902, i, 736).—When a solution containing a salt of an organic acid and also an inorganic salt is electrolysed, the principal product is the alcohol containing one atom of carbon less than the organic acid employed. Under other conditions, the alcohol originally formed may be oxidised to an aldehyde or ketone. Thus, when a solution containing 180 grams of sodium acetate and 200 grams of sodium chlorate per litre is electrolysed at 15—30°, the current-density being 5—20 amperes per sq. dcm., a yield of 34 per cent. of methyl alcohol is obtained. A solution of 240 grams of sodium acetate and 320 grams of sodium chlorate per litre, electrolysed at 20—30° with a current-density of 20—30 amperes per sq. dcm., yields 40 per cent. of formaldehyde and 20 per cent. of methyl alcohol. The preparation of acetone from sodium *iso*butyrate, of β-hydroxypropionic acid from sodium succinate, and of benzaldehyde from sodium phenylacetate is also described.

C. H. D.

Action of Calcium on Alcoholic Ammonia. G. Doby (*Zeit. anorg. Chem.*, 1903, 35, 93—105).—When ammonia is conducted over metallic calcium placed under absolute alcohol, colourless needles and six-sided, prismatic crystals are formed. The needle-shaped crystals are *calcium ethoxide* with alcohol of crystallisation, $Ca(OEt)_2,2EtOH$, and are formed in largest proportion. The same substance is produced by the action of alcohol on calcium-amide, and its formation in the first case is attributed to the two reactions: $Ca + 2NH_3 = Ca(NH_2)_2 + H_2$; $Ca(NH_2)_2 + 4EtOH = Ca(OEt)_2,2EtOH + 2NH_3$. It was proved that no ethylamine is formed in the reaction. Calcium ethoxide is also formed by the action of alcohol on calcium hydride ($CaH_2 + 4EtOH = Ca(OEt)_2,2EtOH + 2H_2$).

Calcium ethoxide closely resembles sodium ethoxide in appearance. It loses its alcohol of crystallisation at 50° and the ethoxide itself undergoes decomposition on prolonged heating at this temperature. It is easily soluble in alcohol, but the solution quickly becomes brown in contact with the air. It is decomposed by water into calcium hydroxide and alcohol. When carbon dioxide is passed through the alcoholic solution, a white precipitate is formed which, in the course of a week or two, is transformed into a yellow, gelatinous mass.

The six-sided, prismatic crystals have the composition represented by the formula CaO,3EtOH, and their formation is due partly to the action of moisture in the original alcohol, and partly to the unavoidable action of the moisture in the air. J. McC.

Theory of Saponification. LUIGI BALBIANO (*Ber.*, 1903, **36**, 1571—1574. Compare Abstr., 1902, i, 450; and Lewkowitsch, this vol., i, 225).—In support of his original theory, the author brings forward the fact that when the hydrolysis of tribenzoin with alkali is interrupted before completion, the products are unaltered tribenzoin, benzoic acid, and glycerol, and no mono- or di-benzoin.

These facts are not in harmony with Lewkowitsch's theory of saponification by stages. J. J. S.

Additive Products of Vinylacetic Acid. ROBERT LESPIEAU (*Compt. rend.*, 1903, **136**, 1265—1266).—When epibromohydrin is heated in a sealed tube with hydrocyanic acid, the bromo-hydroxy-nitrile, $CH_2Br\cdot CH(OH)\cdot CH_2\cdot CN$, is formed, which boils at 149—150° under 12 mm. pressure. When this is treated in chloroform solution with phosphorous bromide, a dibromo-nitrile, $CH_2Br\cdot CHBr\cdot CH_2\cdot CN$, is formed, which boils at 124—126° under 8 mm. pressure and has sp. gr. 2·02 at 0°. When hydrolysed at 110° with hydrobromic acid, *βγ-dibromobutyric acid*, $CH_2Br\cdot CHBr\cdot CH_2\cdot CO_2H$, is formed, which melts at 49—50°. If *iso*crotonic acid were vinylacetic acid, $CH_2\colon CH\cdot CH_2\cdot CO_2H$, it would give the same acid by the addition of bromine, but Michael has shown that the substance $C_4H_6O_2Br_2$, obtained from *iso*crotonic acid and bromine, melts as 58—59°; hence *iso*crotonic acid has not the constitution of vinylacetic acid. *βγ*-Dibromobutyric acid, when warmed with water, easily gives a *γ*-lactone.

If the nitrile is hydrolysed with hydrochloric acid, *γ-chloro-β-bromobutyric acid*, $CH_2Cl\cdot CHBr\cdot CH_2\cdot CO_2H$, is formed, which melts at 49—50°. J. McC.

Reduction of Unsaturated Fatty Acids and their Glycerides. HERFORDER MASCHINENFETT- & OEL-FABRIK, LEPRINCE & SIVEKE (D.R.-P. 141029).—The method of reduction by hydrogen in contact with finely-divided metals, employed by Sabatier and Senderens to reduce unsaturated hydrocarbons, nitro-compounds, &c. (Abstr., 1902, i, 701; ii, 317, 605), may also be applied to the unsaturated fatty acids and their glyceryl esters. The vapour of the unsaturated compound may be passed, together with hydrogen, over the finely-divided contact-metal, or the reaction may take place in the liquid state. Thus, if oleic acid be heated on the water-bath and mixed with finely divided reduced nickel, and a current of hydrogen or water-gas is led through the mass, the oleic acid is entirely converted into stearic acid. Temperature and the quantity of nickel affect only the time required. The nickel is recovered, and may be used again. Olive and linseed oils are in this way converted into hard, tallow-like masses. C. H. D.

Camphocarboxylic Acid. VII. JULIUS W. BRÜHL (*Ber.*, 1903, 36, 1722—1732).—*Amyl* o-*bromocamphocarboxylate*,

$$C_8H_{14}<\begin{matrix}CBr\cdot CO_2\cdot C_5H_{11}\\ |\\ CO\end{matrix},$$

boils at 193·5—194·5° under 13 mm. pressure; the bromination takes place only in sunlight. The *iodo*-compound was also prepared, but was too unstable to be purified.

Methyl o-*bromocamphocarboxylate* crystallises from 80 per cent. alcohol in colourless flakes and sinters and melts at 64—66°. The *iodo*-compound, $C_{12}H_{17}O_3I$, crystallises in glistening, yellow scales, is quite odourless and stable, even on melting, melts at 71—72°, and can be distilled without decomposition in a current of steam; attempts to hydrolyse it with hydrochloric acid gave, however, only camphocarboxylic acid, and sodium methoxide gave methyl camphocarboxylate; the iodo-ester is far less readily hydrolysed than the unsubstituted ester, and the iodo-group is less readily removed than in other iodocamphor compounds.

Ethyl o-*iodocamphocarboxylate*, $C_8H_{14}<\begin{matrix}CI\cdot CO_2Et\\ |\\ CO\end{matrix}$, resembles the methyl ester, sinters at 40°, and melts without decomposition at 42—43°.

Ethyl acetoacetate gives a good yield of the pure α-bromo- and αα-dibromo-esters when brominated in aqueous solution under similar conditions to those used in the case of the camphocarboxylic esters; the iodo-esters are very unstable. Ethyl oxaloacetate gives a mixture of the mono- and dibromo-derivatives. T. M. L.

Formation of Hydrogen Ions from the Methylene Groups of Succinic, Malonic, and Glutaric Acids. RICHARD EHRENFELD (*Zeit. Elektrochem.*, 1903, 9, 335—342).—A boiling solution of succinic acid, when titrated with a solution of potassium hydroxide, using phenolphthalein as indicator, requires about 0·5 per cent. more than the calculated quantity of alkali. Malonic acid behaves in a similar way, both at the ordinary temperature and at 100°. The author considers that this is due to the acid character of the methylene group. The following experiments are made in order to prove the presence of hydrogen ions. Solutions of the normal alkali salts of succinic, malonic, and glutaric acids are mixed with successive drops of very dilute solutions of alkali hydroxide and the conductivity measured. In all cases, a small decrease of conductivity is produced by the addition of the first drops (owing to the replacement of hydrogen ions by sodium ions), followed by an increase. Measurements of the rate of hydrolysis of ethyl acetate by the solutions of the normal salts, and of the potential of a hydrogen electrode in these solutions, led to no definite result. T. E.

Methylation of Ethyl Glutaconate. EDMOND E. BLAISE (*Compt. rend.*, 1903, 136, 1140—1141. Compare Abstr., 1903, i, 400). —*Ethyl* αα*γ-trimethylglutaconate*, produced by methylating ethyl αγ-dimethylglutaconate at 100°, crystallises in large, monoclinic prisms terminated by octahedral pyramids, melts at 150°, and is soluble in

warm, but not in cold, water. The *diethyl hydrogen ester* boils at 139° under 24 mm. pressure. Ethyl trimethylglutaconate is not produced by the action of methyl iodide in presence of sodium ethoxide on ethyl $\alpha\alpha$-dimethylglutaconate.

This difference in behaviour of the two ethyl dimethylglutaconates is explained by assuming that the hydrogen atoms of a methylene group placed between an ethylenic carbon atom and a carboxyl group are replaceable by alkyl groups, whilst a hydrogen atom attached to an ethylenic carbon, even when the latter is contiguous to a carboxyl group, is not. In the formation of ethyl $\alpha\gamma$-dimethylglutaconate and, eventually, of the $\alpha\alpha\gamma$-trimethylglutaconate by the methylation of ethyl glutaconate, it is assumed that the following changes in the position of the ethylenic linkage occur: $CO_2H\cdot CH{:}CH\cdot CH_2\cdot CO_2H \rightarrow CO_2H\cdot CH_2\cdot CH{:}CMe\cdot CO_2H \rightarrow CO_2H\cdot CHMe\cdot CH{:}CMe\cdot CO_2H \rightarrow CO_2H\cdot CMe_2\cdot CH{:}CMe\cdot CO_2H$.

It is further pointed out that only those derivatives of glutaconic ester containing such replaceable hydrogen atoms are coloured yellow by sodium ethoxide. T. A. H.

Action of Organic Acids on the Conductivity of Yellow Molybdic Acid. HERMANN GROSSMANN and HANS KRÄMER (*Ber.*, 1903, 36, 1606—1610. Compare Rosenheim and Bertheim, this vol., ii, 374).—The molecular conductivity of aqueous solutions of molybdic acid dihydrate, $MoO_3,2H_2O$, was determined. The value for $100k$ varies from 0·401 to 0·026, where $v = 16$ and 1024 respectively, thus indicating the formation of an acid with high molecular weight. The conductivity of a mixture of molybdic and succinic acids was less than the sum of the conductivities of the individual acids. Determinations with mixtures of molybdic and malic acids, on the other hand, pointed to the formation of complex acids which are excellent conductors. The large rise of conductivity observed when the proportion of molybdic to malic acid was as 2 : 1 molecules is probably due to the formation of a malodimolybdic acid, more especially since Itzig (Abstr., 1901, i, 580) has shown that the salts of this acid are strongly optically active. Malomolybdic and dimalomolybdic acids undergo hydrolytic dissociation on dilution. Similar relationships were found when tartaric was substituted for malic acid. The compound of molybdic and citric acids is also a good electrolyte. The conductivity of molybdic acid is not, however, raised by the addition of oxalic acid, although it is certain that in this case a complex acid is also formed.
A. McK.

Action of Ethyl Oxalyl Chloride on Mixed Organo-magnesium Compounds. VICTOR GRIGNARD (*Compt. rend.*, 1903, 136, 1200—1201).—When methyl magnesium iodide is added to ethyl oxalyl chloride, reaction takes place according to the equation: $CO_2Et\cdot COCl + 2MeMgI = MgICl + CO_2Et\cdot CMe_2\cdot O\cdot MgI$; then the excess of ethyl oxalyl chloride enters into reaction according to the equation:

$$CO_2Et\cdot CMe_2\cdot O\cdot MgI + COCl\cdot CO_2Et = MgICl + CO_2Et\cdot CMe_2\cdot O\cdot CO\cdot CO_2Et.$$

This oxaloglycollate is a mobile liquid which boils at 246—248°

under 750 mm., and at 128—129° under 13 mm. pressure. The corresponding diethyl compound, $CO_2Et\cdot CEt_2\cdot O\cdot CO\cdot CO_2Et$, is a mobile liquid which boils at 143—144° under 13 mm. pressure. These compounds are very unstable; they always have an acid reaction and are very easily hydrolysed, either by boiling with dilute sodium carbonate solution or by heating under pressure with water at 125°.

If the method be reversed and the ethyl oxalyl chloride (1 mol.) be added slowly to the magnesium compound (2 mols.) cooled by ice, only the COCl group is attacked. In this way, dimethyl-, diethyl-, di*iso*amyl, and diphenyl-glycollic acids have been obtained. From *p*-tolyl magnesium bromide, *p*-tolylglycollic acid, $OH\cdot C(C_6H_4Me)_2\cdot CO_2H$, is obtained in the form of slender needles which melt at 131—132°; it is soluble in all neutral organic solvents except light petroleum.

The reaction can generally be used for the preparation of symmetrically disubstituted glycollic acids. J. McC.

Methylocitric Acid [Methoxytricarballylic Acid]. RICHARD ANSCHÜTZ (*Annalen*, 1903, **327**, 228—240).—The substance previously described as methylocitric acid (Anschütz and Clarke, Abstr., 1899, i, 577) is now shown to be aconitic acid, and to have been formed by the action of alkali on methyl αα-dicarboxyaconitate, which was previously believed to be methyl dicarboxymethoxytricarballylate.

Methyl methoxytricarballylate,

$$CO_2Me\cdot CH_2\cdot C(OMe)(CO_2Me)\cdot CH_2\cdot CO_2Me,$$

is prepared by heating methyl citrate with methyl iodide and silver oxide; it boils at 159—160°, and when hydrolysed with 10 per cent. hydrochloric acid yields methoxytricarballylic acid, which crystallises with H_2O in prismatic forms melting at 98—99°, or when anhydrous at 130—131°; the *silver* salt is an insoluble powder.

Methyl dicarboxyaconitate, $C(CO_2Me)_2{:}C(CO_2Me)\cdot CH(CO_2Me)_2$, is formed when methyl dichloro-oxalate is heated in ethereal solution with methyl sodiomalonate; it melts at 62° and is identical in all respects with the substance previously described as methyl dicarboxymethoxytricarballylate (dicarboxymethylocitrate); the *sodium* derivative is a very hygroscopic, orange powder; the *methylammonium* derivative, prepared by treating the ester in ethereal solution with methylamine, crystallises in orange leaflets melting at 111—111·5°. On hydrolysis with sodium hydroxide or hydrochloric acid, the ester is decomposed, yielding aconitic acid and carbon dioxide. K. J. P. O.

Electrolytic Reduction of Oximes to Amines. C. F. BOEHRINGER & SOEHNE (D.R.-P. 141346).—Oximes may be reduced to amines by electrolysis in sulphuric acid solution (compare Tafel and Pfeffermann, Abstr., 1902, i, 498), cathodes of pure lead or mercury being employed, and the temperature being maintained below 20°. Acetoxime is dissolved in 50 per cent. sulphuric acid in the cathode-cell, and electrolysed with a current-density of 16 amperes per sq. dcm. Benzaldoxime is similarly reduced to benzylamine. Benzophenoneoxime, dissolved in 60 per cent. sulphuric acid, requires a

current-density of 12 amperes per sq. dcm., using a mercury cathode of 10 sq. dcm. area per litre. In this case, the temperature may rise to 25—30°. Camphoroxime, dissolved in 30 per cent. sulphuric acid, is similarly reduced to bornylamine. C. H. D.

Biochemical Transformation of Carbohydrates of the *d*-Series into those of the *l*-Series. ERNST SALKOWSKI and CARL NEUBERG (*Zeit. physiol. Chem.*, 1903, **37**, 464—466).—The conversion of *d*-galactonic acid into *l*-arabinose, of *d*-idonic acid into *l*-xylose by the loss of carbon dioxide by processes of fermentation, and of *d*-galactose into *l*-sorbinose (Lobry de Bruyn and Alberda van Ekenstein, Abstr., 1900, i, 208, 332) are offered as further examples of this class of transformation (compare Küster, this vol., i, 402). J. J. S.

Crystallised *i*-Mannose. CARL NEUBERG and PAUL MAYER (*Zeit. physiol. Chem.*, 1903, **37**, 545—547).—*i*-Mannose has been obtained in a crystalline form from its phenylhydrazone. It crystallises from a mixture of absolute methyl alcohol and anhydrous ether in small, transparent, rhombic prisms melting at 132—133° (corr.) and possessing the same solubility as the *d*-compound. All the data point to the fact that the *i*-substance is an externally compensated agglomeration and not a true racemic compound. J. J. S.

Successive Action of Acids and Soluble Ferments on Complex Polysaccharides. EMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1903, **136**, 1143—1146. Compare Abstr., 1902, i, 744, and this vol., i, 378, 452).—Confirmation of the view previously expressed by the authors that at least two soluble ferments are necessary to effect complete hydrolysis of complex sugars to hexoses has been obtained by investigating the successive action of dilute sulphuric acid and the seminase contained in malted lucerne seeds on the mannans of the seeds of *Phœnix canariensis* (Abstr., 1901, ii, 619) and *Phytelephas macrocarpa*. No mannose is produced by macerating the ground seeds of these plants in dilute sulphuric acid for 24 hours, but a small quantity of this sugar is obtained in the course of 48 hours by adding to such extracts, previously neutralised with chalk, a small quantity of malted lucerne grains. The action of the sulphuric acid is not merely solvent, since the residue insoluble in the dilute acid, when washed with water and mixed with seminase, affords a quantity of mannose. It follows that the seeds of *Phœnix canariensis* and *Phytelephas macrocarpa* must on germination produce a ferment complementary in its action to seminase. T. A. H.

Behaviour of the Ammonium Salts of some Amino-acids in Aqueous or Sugar Solutions on Heating. KARL ANDRLÍK (*Zeit. Zuckerind. Böhm.*, 1903, **27**, 437—445).—The author finds that solutions of the ammonium salts of aspartic and glutamic acids, tyrosine, and leucine, when boiled either with or without sugar, lose ammonia—the first two partially, but the last two completely. If the

solutions are alkaline to phenolphthalein, they become acid on boiling, the acidity increasing with the amount of evaporation. The acid-reacting ammonium salts of aspartic and glutamic acids bring about inversion of sucrose solutions on boiling, the amount of change increasing with the concentration. When evaporated under reduced pressure, solutions of the alkaline ammonium salts of aspartic and glutamic acids lose ammonia, but only slight inversion of sucrose occurs, owing to the low temperature. The ammonium salts of tyrosine and leucine only bring about a small amount of inversion in sugar solutions, although they completely lose their ammonia. The acidity of beet juices, which in some cases lose their alkalinity on evaporation, is to be explained by the presence of ammonium salts of amino-acids; these lose ammonia, yielding an acid-reacting ammonium salt which causes decomposition of the sucrose. T. H. P.

New Class of Narcotics. EMIL FISCHER and VON MERING (*Chem. Centr.*, 1903, i, 1155; from *Therapie der Gegenwart*, 1903, March).—*a-Ethylbutyrylcarbamide*, $CHEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$, *diethylmalonylcarbamide*, $CEt_2<{CO\cdot NH \atop CO\cdot NH}>CO$, and *dipropylmalonylcarbamide*, behave as narcotics. The first named is as powerful as sulphonal, whilst the action of the last is four times as strong. Diethylmalonylcarbamide (*versonal*) occupies an intermediate position in this respect, and for other reasons is also the most suitable for practical application. It forms colourless crystals, has a faintly bitter taste, melts at 191°, and is soluble in 145 parts of water at 20°, and in 12 of boiling water. E. W. W.

Mode of Fission of Mixed Organo-magnesium Compounds. Action of Ethylene Oxide. VICTOR GRIGNARD (*Compt. rend.*, 1903, 136, 1260—1262).—When a well-cooled (– 15°) solution of ethylene oxide in ether is added to cold ethyl magnesium bromide, and, after keeping for 24 hours, the ether is distilled off, a reaction takes place with development of much heat, and when the product is distilled in steam *n*-butyl alcohol is obtained. In the same way, using *iso*amyl magnesium bromide, iso*heptyl* alcohol, $CHMe_2\cdot[CH_2]_3\cdot CH_2\cdot OH$, was obtained as a mobile liquid, which boils at 167—169°, has a sp. gr. 0·8249 at 11·5°/4°, and $n_D = 1·42538$. Its *acetate* has a fruity odour, boils at 183—185°, has a sp. gr. 0·8757 at 11·7°/4°, and $n_D = 1·41739$.

Blaise (Abstr., 1902, i, 357) obtained glycol monobromohydrin by the action of ethylene oxide on ethyl magnesium bromide. The author assumes as first phase of the reaction the formation (on account of the quadrivalent property of the oxygen of ethylene oxide) of

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}>O<{R \atop MgBr}.$$

When this is treated with water, the liberated ethylene oxide may act on the magnesium salt formed, and thus give the monobromohydrin of glycol. But if the solvent ether is removed, the temperature may rise, and the first product suffers rearrangement into $R\cdot CH_2\cdot CH_2\cdot OMgBr$, which decomposes normally with water, giving an alcohol. J. McC.

Syntheses of Benzene Hydrocarbons by Reduction of Groupings Containing Oxygen. I. August Klages (*Ber.*, 1903, 36, 1628—1631).—The method of preparing benzene hydrocarbons by introduction of groupings containing oxygen into the benzene ring and subsequent reduction has seldom been employed. Hydriodic acid is the usual reducing agent in such cases, but the yields of hydrocarbons are slight. Production of polymerised styrenes probably takes place; benzophenone, for example, which is incapable of styrene formation, is readily reduced to derivatives of diphenylmethane. Further, the iodides of the carbinols, formed initially, are reducible with difficulty by hydrogen iodide.

Sodium amalgam, zinc and alkali, or zinc and acetic acid do not form hydrocarbons from aldehydes and ketones, but convert them into carbinols. When the iodides, obtained by treatment of the latter with hydrogen iodide and acetic acid, are heated with zinc dust, an action of the following nature may take place, namely: $CHMePhI \longrightarrow CHMePh \cdot CHMePh + I_2$, or the reduction may proceed normally, thus: $CMePh_2I \longrightarrow CHMePh_2$.

Sodium and alcohol convert aromatic ketones into derivatives of diphenylmethane; fatty aromatic ketones are reduced to carbinols. Carbinols may be readily obtained from aldehydes, acids, or ketones of aromatic hydrocarbons, either by reduction or by Grignard's method. Carbinols are easily converted into styrenes (Klages, Abstr., 1902, i, 666, &c.), which can then be reduced to the synthetical benzene hydrocarbons, containing a larger number of carbon atoms than the original hydrocarbons. A. McK.

Behaviour of the Vinyl Group on Reduction. Ethylated Benzenes. August Klages and Rudolf Keil (*Ber.*, 1903, 36, 1632—1645).—Ethylbenzene can be prepared by reducing styrene with sodium ethoxide in boiling ethyl alcoholic solution. Styrene dibromide melts at 74°, 1-ethyl-4-vinylbenzene dibromide at 66°. When 1-ethyl-4-vinylbenzene is reduced by sodium ethoxide, it yields *p*-diethylbenzene with a sp. gr. 0·8675 at 14°/4° and n_D 1·4978. Its acetyl derivative, boiling at 151—152° under 17 mm. pressure and having the sp. gr. 0·9687 at 16°/4°, gives, on reduction, 1 : 4-*diethyl*-2-*vinylbenzene*, boiling at 96—97° under 12 mm. pressure, which, when further reduced, forms 1 : 2 : 4-*triethylbenzene*, a colourless liquid boiling at 99° under 15 mm. pressure and having the sp. gr. 0·8119 at 17°/4° and n_D 1·4983. Its *tribromo*-derivative crystallises in needles melting at 88—90°. The symmetrical triethylbenzene has a lower boiling point and sp. gr. than its unsymmetrical isomeride. The latter, when acetylated, forms 5-*acetyl*-1 : 2 : 4-*triethylbenzene*, a colourless syrup boiling at 146° under 13 mm. pressure and having the sp. gr. 0·9634 at 12°/4°. On reduction, 5-*ethylol*-1 : 2 : 4-*triethylbenzene* (2 : 4 : 6-*triethylphenylmethylcarbinol*), $C_6H_2Et_3 \cdot CHMe \cdot OH$, is formed; it boils at 149° under 13 mm. pressure and crystallises from alcohol in colourless, transparent needles melting at 45°; its *phenylurethane* melts at 75—76°. By reduction of the corresponding styrene, 1 : 2 : 4 : 5-tetraethylbenzene, an oil boiling at 248° under

755 mm. pressure and having the sp. gr. 0·8884 at 16°/4°, and n_D 1·5041, is formed. Its tetrabromide melts at 113°.

In analogous manner, the ethyl group can be introduced into benzene homologues. p-*Tolylmethylcarbinol*, prepared from *p*-tolyl methyl ketone, boils at 120° under 19 mm. pressure and has the sp. gr. 0·9668 at 15·5°/4°; its *phenylurethane* melts at 95—96°; its chloride forms with pyridine an additive compound,

$$C_5H_5 \vdots NCl \cdot CHMe \cdot C_6H_4Me,$$

from which, by moist silver oxide, the free base may be obtained; the *picrate* of this melts at 116—117° and the *platinichloride* at 208°. 1-Methyl-4-vinylbenzene boils at 63° under 15 mm. pressure; it has the sp. gr. 0·8978 at 16°/4° and n_D 1·5306; its dibromide melts at 45°; it forms, on reduction, 1-methyl-4-ethylbenzene, a colourless oil boiling at 162·5° and having the sp. gr. 0·8690 at 14°/4° and n_D 1·494. When 1 : 3-dimethyl-4-chloroethylbenzene is heated with pyridine at 120°, 1 : 3-dimethyl-4-vinylbenzene is formed. The pyridylium chloride, $C_5H_5 \vdots NCl \cdot CHMe \cdot C_6H_3Me_2$, melts at 53°, whilst the analogous bromide melts at 144—145°. The free base forms a picrate melting at 161—162°. 1 : 3-Dimethyl-4-vinylbenzene is a colourless oil boiling at 79—80° under 12 mm. pressure and having the sp. gr. 0·9022 at 21·5°/4° and n_D 1·5214. 1 : 3-Dimethyl-4-ethylbenzene, prepared from it, boils at 67—68° under 12 mm. pressure and has the sp. gr. 0·8772 at 16°/4° and n_D 1·5033. Its tribromo-derivative melts at 135°. 2-*Ethylol*-1 : 4-*dimethylbenzene* (p-*xylylmethylcarbinol*) boils at 114° under 12 mm. pressure. 1 : 4-Dimethyl-2-vinylbenzene boils at 69° under 10 mm. pressure and forms a dibromide melting at 55°. 1 : 4-Dimethyl-2-ethylbenzene boils at 64° under 10 mm. pressure and has the sp. gr. 0·8824 at 17°/4° and n_D 1·5026; its tribromo-derivative melts at 89°. 1-*iso*Propyl-4-vinylbenzene is an oil of a lemon odour and boils at 76° under 10 mm. pressure. It forms 1-ethyl-4-*iso*propylbenzene boiling at 72° under 10 mm. pressure and having the sp. gr. 0·8606 at 16°/4° and n_D 1·4928; its tetrabromo-derivative melts at 246°. The magnesium, zinc, and barium salts of the corresponding sulphonic acid are described. 1 : 2 : 4-*Trimethyl*-5-*ethylbenzene* boils at 88° under 13 mm. pressure and has the sp. gr. 0·8890 at 14°/4° and n_D 1·5077. Its sulphonic acid melts at 70—72°. 1 : 3 : 5-Trimethyl-2-chloroethylbenzene forms a pyridylium chloride melting at 107—108° and giving a platinichloride melting and decomposing at 198°. 1 : 3 : 5-Trimethyl-2-vinylbenzene boils at 206—207° under 755 mm. pressure and, on reduction, gives 1 : 3 : 5-trimethyl-2-ethylbenzene, boiling at 93—94° under 16 mm. pressure, and at 207—208° under 755 mm. pressure. Its sulphonic acid melts at 78—80°.

A. McK.

Electrolytic Oxidation of Toluene-*p*-sulphonic Acid. J. Šebor (*Zeit. Elektrochem.*, 1903, 9, 370—373).—At a platinum anode in 10 or 20 per cent. sulphuric acid, no oxidation takes place at the ordinary temperature, whilst at 80° a slight amount occurs. When a lead anode is used at about 70°, a large portion (80—90 per cent.) of the electrolytic oxygen is absorbed, and *p*-sulphobenzoic acid is formed. The yield is, however, small, a considerable portion of the acid being further oxidised.

T. E.

Reactions of Aromatic Nitrothiocarbamides. Karl Elbs and H. Schlemmer (*J. pr. Chem.*, 1903, [ii], 67, 479—480. Compare Hugershoff, this vol., i, 477).—When boiled with alcohol, *m*-nitrodiphenylthiocarbamide is partly decomposed into *m*-nitrophenylthiocarbimide and aniline, and *m*-nitroaniline and phenylthiocarbimide. Diphenylthiocarbamide and *m*-dinitrodiphenylthiocarbamide are formed by combination of the decomposition products.

Similar results have been obtained with *m*-nitrophenyl-*o*-tolyl- and *m*-nitrophenyl-*p*-tolyl-thiocarbamides. G. Y.

[Preparation of a New Aromatic Dithiocarbamide.] Kalle & Co. (D.R.-P. 139429).—1 : 3-*Naphthylenediamine*-6-*sulphonic acid dithiocarbamide* is prepared by mixing 1 : 3-naphthylenediamine-6-sulphonic acid with hydrochloric acid, adding ammonium thiocyanate, and, after evaporating to dryness, heating the residue at 130°. By dissolving in water and salting out, the sodium salt is obtained in very soluble yellow crystals. The free acid is insoluble in alcohol, but dissolves in water to a yellow solution. C. H. D.

Separation of *p*- and *m*-Cresols. Firma Rud. Rütgers (D.R.-P. 141421).—The method for the separation of *p*- and *m*-cresols described in a former patent (this vol., i, 479) may be modified by using dry acid oxalates or quadroxalates in place of anhydrous oxalic acid. At 100°, these acid salts yield the normal metallic oxalates which then act as dehydrating agents and combine with the water produced in the reaction between *p*-cresol and the acid oxalate, thus preventing the hydrolysis of the oxalic ester. The employment of a vacuum is in this way rendered unnecessary. The mixture of *p*-tolyl oxalate with hydrated metallic oxalate is filtered off and distilled in steam, when *p*-cresol passes over, whilst the residue contains a solution of the acid oxalate originally used. C. H. D.

Decomposition of *p*-*ter*.-Butyl- and *p*-*ter*.-Amyl-phenols. Richard Anschütz and Georg Rauff (*Annalen*, 1903, 327, 201—210). —*p*-*ter*.-Butylphenol was oxidised in alkaline solution with dilute permanganate and the resulting solution extracted with ether, after filtering and precipitating the oxalic acid. The oily mixture of acids contained in the extract was distilled under reduced pressure, when a mixture of trimethylpyruvic acid and trimethylacetic acid distilled over; the former was recognised by conversion into the phenylhydrazone (m. p. 153°), and the latter in the mother liquor from the hydrazone.

On oxidising with permanganate Liebmann's *iso*amylphenol (Abstr., 1882, 171, 727) obtained by treating phenol and *iso*amyl alcohol with zinc chloride, a liquid acid mixture was formed, which was distilled under reduced pressure. In this mixture, dimethylethylpyruvic acid can be recognised by conversion into its *phenylhydrazone*, which crystallises in leaflets melting at 146°. This acid can be obtained in a pure state by converting the mixture into calcium salts and extracting with water, when the soluble calcium salt of dimethylethylacetic acid dissolves; *calcium dimethylethylpyruvate* forms with H_2O a white, crystal-

line precipitate; the *acid*, $CMe_2Et \cdot CO \cdot CO_2H$, prepared from this salt is a colourless liquid boiling at 86° under 15 mm. pressure, and is readily oxidised by chromic acid to dimethylethylacetic acid, which boils at 85° under 13 mm. pressure. K. J. P. O.

2 : 6-Dinitro-4-*ter.*-amylphenol and its Transformation Products. RICHARD ANSCHÜTZ and GEORG RAUFF (*Annalen*, 1903, 327, 211—217).—2 : 6-*Dinitro*-4-ter.-*amylphenol*,

$$CMe_2Et \cdot C_6H_2(NO_2)_2 \cdot OH,$$

is prepared by adding 65 per cent. nitric acid to an acetic acid solution of *p-ter.*-amylphenol; it forms yellow leaflets which explode on heating and is converted by nitric acid into picric acid; the *silver* salt is a red, crystalline powder; the *ammonium* salt crystallises in brown leaflets. The *methyl ether* prepared from the silver salt melts at 39°.

2 : 6-*Dinitro*-4-ter.-*amylaniline* is formed when the phenol is heated with concentrated ammonia under pressure at 175°, and melts at 71—72°. 6-*Nitro*-4-ter.-*amyl*-o-*phenylenediamine*, prepared by reducing the foregoing compound with alcoholic ammonium sulphide, separates in red, plate-like crystals melting at 82—83°, and when treated with benzil yields the *quinoxaline*, $C_5H_{11} \cdot C_6H_2(NO_2) < \begin{matrix} N:CPh \\ N:CPh \end{matrix}$, which crystallises in needles melting at 189—190°. On reducing the dinitroaniline with stannous chloride, 1 : 2 : 6-*triamino*-4-ter.-*amylphenol* is obtained; it crystallises in leaflets melting at 149°, and is very readily oxidised by the air. K. J. P. O.

Formation of *p-ter.*-Amylphenol and *ter.*-Amylbenzene. RICHARD ANSCHÜTZ and H. BECKERHOFF (*Annalen*, 1903, 327, 218—227). —The methods of preparing tertiary *p*-amylphenol have been investigated, with the result that it has been shown that the phenol obtained by Königs (Abstr., 1891, 208) from *iso*amylene and phenol, sulphuric acid being used as the condensing agent, is identical with that obtained from amylaniline by Calm (Abstr., 1882, 1284).

In both cases, the phenol melted at 93° and yielded a benzoyl derivative melting at 60°, which crystallised in the rhombic system [$a : b : c = 0{\cdot}69469 : 1 : 1{\cdot}22257$]. *Acetyl*-p-ter.-*amylaniline*, prepared from *p-ter.*-amylaniline, obtained by Calm's method from aniline, amylene hydrate and zinc chloride, crystallises in leaflets melting at 138—139°; the corresponding *benzoyl* derivative melts at 158°. *ter.*-Amylbenzene can be easily prepared from the aniline by treatment of the diazo-compound with alkaline solution of stannous chloride. When nitrated in acetic acid solution, a *mononitro*-derivative is obtained, which is an oil boiling at 152—154° under 15 mm. pressure and having a sp. gr. 1·2656 at 20°/4°; this mononitro-compound is mainly the *para*-derivative. K. J. P. O.

***p*-Chloro-*o*-nitroanisole.** FRÉDÉRIC REVERDIN (*Ber.*, 1903, 36, 1689—1690).—*p*-Chloro-*o*-nitroanisole, prepared by nitrating *p*-chloroanisole (Reverdin, Abstr., 1897, i, 27; Reverdin and Eckhard, Abstr.,

1900, i, 28), melts at 97·5° (corr.), and the compound prepared from nitro-*p*-dichlorobenzene by the action of methyl-alcoholic soda or potash (D.R.-P. 140133, this vol., i, 478) is identical and not isomeric with it.

T. M. L.

Preparation of Aminohydroxyphenanthrene. JULIUS SCHMIDT (D.R.-P. 141422. Compare Abstr., 1902, i, 757).—9-Amino-10-hydroxyphenanthrene, produced from phenanthraquinone by reduction either with hydrogen sulphide or excess of stannous chloride, forms a *hydrochloride* crystallising in white needles, which become red above 120° and gradually char on further heating. This salt is converted into hydrophenanthraquinone by heating with water or dilute acids, whilst oxidising agents (nitric, nitrous, or chromic acids) and alkalis convert it into phenanthraquinone. It can therefore be purified only by crystallisation from fuming hydrochloric acid, or by precipitation from an alcoholic solution by fuming hydrochloric acid.

C. H. D.

Does Cholesterol occur in Olive Oil? AUGUSTUS H. GILL and CHARLES G. TUFTS (*J. Amer. Chem. Soc.*, 1903, **25**, 498—503. Compare this vol., i, 417).—From a Californian oil prepared from fully ripened olives, an alcohol was obtained melting at 134—134·5°. After some days, the melting point altered to 132—133°. The crystalline form closely resembled that of the sitosterol from maize oil. A table is given showing the melting points given by various investigators for phytosterol, sitosterol, cholesterol, and the product from olive oil, and their respective esters. The conclusion is drawn that the alcohol from olive oil is not cholesterol.

A. McK.

Synthesis of Quinols. EUGEN BAMBERGER and LOUIS BLANGEY (*Ber.*, 1903, **36**, 1625—1628).—Quinols prepared from *p*-methylated arylhydroxylamines by the action of dilute sulphuric acid are represented by the scheme $\begin{matrix}Me\\OH\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}\dot{C}{:}\dot{C}\\ \dot{C}{:}\dot{C}\end{matrix}\!\!>\!CO$ (Bamberger, Abstr., 1901, i, 140; 1902, i, 509; Zincke, Abstr., 1901, i, 204; Auwers, Abstr., 1902, i, 216). It is now shown that quinols can be prepared synthetically from quinones by Grignard's magnesium methyl iodide. Toluquinone forms *o*-dimethylquinol isomeric with the *m*-isomeride of Bamberger and Brady (Abstr., 1901, i, 142). *o*-Dimethylquinol interacts with *p*-nitrophenylhydrazine to form the azo-compound, $CMe\!<\!\!\begin{matrix}CMe\cdot CH\\CH{=}CH\end{matrix}\!\!>\!C\cdot N{:}N\cdot C_6H_4\cdot NO_2$, which crystallises in highly lustrous, bright orange-red needles melting at 135·5°. The same azo-compound is also formed from 1 : 2-dimethyl-4-aminobenzene and *p*-nitronitrosobenzene.

p-Xyloquinone and magnesium methyl iodide form 1 : 2 : 5-trimethylquinol, the constitution of which is further determined by its formation from *ψ*-cumenol by Caro's acid. It forms hard, vitreous needles melting at 116—116·5°.

The yield of quinols was small.

A. McK.

[Derivatives of 4 : 4′-Dimethoxydiphenylmethane.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 140690).—3 : 3′-*Dinitro*-4 : 4′-*dimethoxydiphenylmethane*, $CH_2[C_6H_3(NO_2)\cdot OMe]_2$, prepared by condensing *o*-nitroanisole with formaldehyde (compare D.R.-P. 72490), separates from a mixture of alcohol and benzene in greyish-white crystals, which melt at 160° and dissolve in benzene and chloroform, and are sparingly soluble in alcohol. On reduction, it yields 3 : 3′-*diamino*-4 : 4′-*dimethoxydiphenylmethane*, which crystallises from boiling light petroleum, in which it is only sparingly soluble, in small, white needles melting at 107°. It is insoluble in water, but dissolves readily in alcohol, benzene, chloroform, and dilute mineral acids. Its *tetrazonium* compound combines with β-naphthol to form a fast red azo-dye. C. H. D.

Phenol-ethers. II. HERMANN THOMS (*Ber.*, 1900, 36, 1714—1721).—2 : 3 : 5-*Trimethoxy*-1-*propylbenzene*, $C_6H_2Pr(OMe)_3$, prepared by methylating 3-hydroxy-2 : 5-dimethoxy-1-propylbenzene (Ciamician and Silber, Abstr., 1890, 1294), boils at 144—146° under 12 mm. pressure.

The 4-*nitro*-derivative crystallises from 70 per cent. alcohol in yellow, glistening needles, melts at 65°, and can be reduced with aluminium amalgam. 6-*Methoxy*-2-*propylquinone*, $OMe\cdot C_6H_2PrO_2$, a bye-product in the nitration, crystallises from water in stout, dark lemon-yellow crystals and melts at 79°. The *quinol*,

$$OMe\cdot C_6H_2Pr(OH)_2,$$

crystallises from water in minute, colourless needles, becomes strongly electrified when rubbed, and melts at 105°.

2 : 5-*Dimethoxy*-3-*ethoxy*-1-*propylbenzene*, $C_6H_2Pr(OMe)_2\cdot OEt$, boils at 147—149° under 12 mm. pressure. The 4-*nitro*-derivative crystallises from 70 per cent. alcohol in small, pale yellow needles and melts at 75°. 6-*Ethoxy*-2-*propylquinol*, $OEt\cdot C_6H_2Pr(OH)_2$, separates from water in colourless, silky flakes or needles and melts at 143°.

2 : 5-*Dimethoxy*-3-*n*-*propyloxy*-1-*propylbenzene*, $C_6H_2Pr(OMe)_2\cdot OPr^a$, boils at 156—157° under 12 mm. pressure. The 4-*nitro*-derivative crystallises from 70 per cent. alcohol in pale yellow needles and melts at 68°. 6-*Propyloxy*-2-*propylquinol*, $OPr\cdot C_6H_2Pr(OH)_2$, separates from water in colourless, felted needles and melts at 102°. T. M. L.

Preparation of Alkaline Additive Products of Aromatic Polyhydroxy-compounds. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 141101).—Aromatic polyhydroxy-compounds react readily with fatty amines when the two substances are fused together or dissolved in a suitable solvent. The reagents condense in molecular proportion, and the products are stable compounds with an alkaline reaction, which may be applied as photographic developers. *Dimethylamine-pyrogallol*, $C_6H_3(OH)_3,NHMe_2$, prepared in aqueous solution, crystallises in prisms, melts at 163°, dissolves readily in water, less readily in alcohol, and is insoluble in ether. It is stable when kept in a closed vessel, but decomposes on long boiling. *Trimethylamine-pyrogallol*, prepared in alcoholic solution, melts at

160°. *Dimethylamine-resorcinol*, precipitated from ethereal solution by light petroleum, forms prisms melting at 82°. *Dimethylamine-catechol*, prisms, melts at 115°; *methylamine-catechol* melts at 98°. *Dimethylamine-* and *methylamine-quinol* form prisms melting at 132° and 110° respectively. The *dimethylamine* derivative of *methyl gallate* melts at 164°, and that of *ethyl gallate* crystallises from water and melts at 79°, but after crystallisation from alcohol loses water and melts at about 122°. The *dimethylamine* derivative of *methyl* s-*dihydroxybenzoate* melts at 95°, and that of *gallacetophenone* at 156°. C. H. D.

Action of Alkaline-earth Bases on the Alkaline-earth Salts of Pyrogallolsulphonic Acids. MARCEL DELAGE (*Compt. rend.*, 1903, **136**, 1202—1204. Compare Abstr., 1901, i, 643, and this vol., i, 416).—When calcium hydroxide in suspension in water is added to an aqueous solution of calcium pyrogallolsulphonate, the solution becomes coloured when vigorously shaken. Alcohol does not cause precipitation, but when ether is added to the alcoholic solution a blue, flocculent precipitate of the oxidised product of tricalcium pyrogallolsulphonate is obtained. Its solution in water turns brown on keeping, but is not altered by boiling. Similarly, from calcium hydroxide and calcium pyrogalloldisulphonate, the oxidised product of tetracalcium pyrogalloldisulphonate is obtained as a blue powder; it is insoluble in alcohol, but soluble in water to a violet solution which becomes brown in the air.

From strontium hydroxide and strontium pyrogallolsulphonate, the violet oxidised product of tristrontium pyrogallolsulphonate is formed, which is almost insoluble in water. From strontium pyrogalloldisulphonate, a blue powder is obtained, which is the oxidised product of tetrastrontium pyrogalloldisulphonate.

Barium hydroxide and barium pyrogallolsulphonate in contact with air give a blue, insoluble oxidation product of tribarium pyrogallolsulphonate, whilst with barium pyrogalloldisulphonate a blue, insoluble oxidation product of tetrabarium pyrogalloldisulphonate is produced.

The analytical results are discussed. J. McC.

Formation of Acid Esters. RUDOLF WEGSCHEIDER (*Ber.*, 1903, **36**, 1544—1549. Compare Abstr., 1902, i, 618).—A detailed reply to Kahn's criticisms (this vol., i, 93). W. A. D.

***p*-Aminobenzonitrile.** MARSTON T. BOGERT and LOTHAIR KOHNSTAMM (*J. Amer. Chem. Soc.*, 1903, **25**, 478—483).—p-*Aminobenzonitrile*, prepared by the reduction of *p*-nitrobenzonitrile by various methods, melts at 85·5—86° (corr.) and is monoclinic [$a : b : c = 1·7475 : 1 : 1·4573$. $\beta = 47°50'$]. Its *acetyl* derivative forms fine white needles melting at 200°, whilst its *propionyl* derivative melts at 169°. When it is warmed at 50° with alkaline hydrogen peroxide solution, it forms *p*-aminobenzamide. *p*-Aminobenzthiamide melts at 172° (Engler gave 170°).

A. McK.

Hippuronitrile and some Substituted Hippuronitriles. August Klages and O. Haack (*Ber.*, 1903, 36, 1646—1649).—The method for the preparation of hippuronitrile from aminoacetonitrile and benzoyl chloride (see Abstr., 1902, i, 354) may be modified by the use of the acid sulphate in place of the free base. The yield is also increased by diluting the benzoyl chloride with benzene. In this form, the method may be employed for the synthesis of a number of derivatives of hippuronitrile.

p-*Bromohippuronitrile*, $C_6H_4Br{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CN$, from aminoacetonitrile sulphate and *p*-bromobenzoyl chloride, crystallises from alcohol in thick, glistening needles, melts at 174°, and dissolves readily in hot alcohol, sparingly in ether or benzene. Boiling with alcoholic hydrogen chloride converts it into *ethyl* p-*bromohippurate*, crystallising from light petroleum in needles melting at 123° and dissolving readily in hot water or alcohol. On hydrolysis, *p*-bromohippuric acid is obtained in colourless needles melting at 162°, readily soluble in hot water or alcohol.

m-*Nitrohippuronitrile*, from *m*-nitrobenzoyl chloride, separates from alcohol in colourless leaflets, melts at 118° and dissolves readily in alcohol or benzene. *m*-Nitrohippuric acid melts at 165° (compare Conrad, this Journal, 1877, ii, 484).

p-*Nitrohippuronitrile* crystallises from alcohol in needles melting at 145°, readily soluble in alcohol and glacial acetic acid, sparingly so in ether or light petroleum. p-*Methylhippuronitrile*, from *p*-toluoyl chloride, separates from water in flat needles, melts at 153° and dissolves in alcohol, glacial acetic acid, and benzene, sparingly in ether or light petroleum. *Ethyl* p-*methylhippurate* melts at 71° and dissolves readily in hot water, alcohol, ether, and light petroleum.

Phenylaceturonitrile, $CH_2Ph{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CN$, from phenylacetyl chloride, forms thick, glistening needles melting at 90·5° and sparingly soluble in hot water. *Ethyl phenylaceturate* forms colourless needles melting at 82°. C. H. D.

Reduction of *o*-Nitroacetophenone. The First Indigo Synthesis. Eugen Bamberger and Franz Elger (*Ber.*, 1903, 36, 1611—1625).—Camps has shown (this vol., i, 33) that in the first indigo synthesis (Engler and Emmerling, *Ber.*, 1870, 3, 885; Abstr., 1895, i, 231) *o*-nitroacetophenone is first reduced by zinc dust and soda lime to an oil, to which he assigns the constitution $C_{16}H_{16}O_2N_2$, which is converted into indigo on being strongly heated. The authors observed that this oil possessed physical and chemical properties similar to those of anthranil, and find that it is methylanthranil, C_8H_7ON. Its formation from *o*-nitroacetophenone is analogous to that of anthranil from *o*-nitrobenzaldehyde, intermediate hydroxylamine derivatives being produced in both cases (compare Bamberger, this vol., i, 432; *Ber.*, 1903, 36, 826). When the oil is strongly heated, it undergoes intramolecular rearrangement into indoxyl, which is then transformed into indigo.

Methylanthranil, $C_6H_4{<}\substack{CMe\\ |\\ N}{>}O$, was prepared by reducing *o*-nitro-

acetophenone with zinc and ammonium chloride. The crude product was converted into the crystalline *mercurichloride*, $C_8H_7ON,1\frac{1}{2}HgCl_2$, which forms white, silky needles, and, when quickly heated, melts at 169·5°; when it is distilled with steam, pure methylanthranil is formed, a colourless, clear oil boiling at 110·5—111° under 10 mm. pressure, and with an odour resembling that of anthranil. It solidifies in a freezing mixture to white, glassy needles. Its molecular weight was determined by the ebullioscopic and cryoscopic methods.

From the original mixture, from which the crude methylanthranil had been removed, a crystalline product melting at 125—131° was obtained. It consisted mainly of *m*-azoxyacetophenone, formed from the *m*-nitroacetophenone originally present along with the *o*-isomeride. Pure m-*azoxyacetophenone*, $(C_6H_4Ac)_2N_2O$, is easily prepared by reducing *m*-nitroacetophenone to hydroxylaminoacetophenone by zinc dust and ammonium chloride, and then oxidising the latter by leaving it exposed to air until it ceases to reduce Fehling's solution; it melts at 137·5°. Methylanthranil may also be very conveniently prepared by using tin and acetic acid as the reducing agent.

Methylanthranil dichloride, $C_6H_4<\begin{matrix}CMe\\|\\NCl_2\end{matrix}>O$, prepared by the action of sodium nitrite on a mixture of methylanthranil and concentrated hydrochloric acid, crystallises in strongly refracting, vitreous prisms melting at 101—101·5°. The filtrate, from which the dichloride had been separated, contained the diazonium salt of *o*-aminoacetophenone, $C_6H_4Ac\cdot N_2Cl$, which was proved by the formation with alkaline β-naphthol of an azo-dye melting at 198·5—199°, and also by the formation of *o*-oxyacetophenone when the solution was warmed.

Chloromethylanthranil, $C_6H_3Cl<\begin{matrix}CMe\\|\\N\end{matrix}>O$, prepared by boiling the dichloride with water and then distilling in steam, crystallises from light petroleum in white, silky needles melting at 97·5—98°. Its *mercurichloride*, $C_8H_6ONCl,1\frac{1}{2}HgCl_2$, separates in white, silky needles melting at 183·5°. When chlorine is passed into a solution of methylanthranil in concentrated hydrochloric acid, a mixture of the two chlorine derivatives is formed.

Methylanthranil, when heated, undergoes rearrangement into indoxyl, which then yields indigo.

That indoxyl is present along with indigo when methylanthranil is heated, was proved by its isolation and its subsequent conversion into phenylazoindoxyl by the aid of diazonium chloride. A. McK.

Preparation of Phthalic and Benzoic Acids. Basler Chemische Fabrik (D.R.-P. 140999).—The process for the preparation of phthalic and benzoic acids from naphthols by heating with alkali hydroxides and metallic oxides (compare this vol., i, 487) may be extended to other substitution derivatives of naphthalene, such as nitronaphthalenes, naphthylamines, nitronaphthols, nitrosonaphthols, and naphtholsulphonic acids. Naphthalenesulphonic acids may also be employed without previous fusion with alkali hydroxide, but a smaller yield is then obtained. C. H. D.

A Characteristic Property of Gallein. RICHARD MEYER (*Ber.*, 1903, 36, 1561—1565).—Gilbody and Perkin (Trans., 1902, 81, 245) have recently called into question the author's statement that the dry distillation of hæmatoxylin gives a mixture of phenols which, when fused with phthalic anhydride, shows both the fluorescein and gallein reactions with aqueous sodium hydroxide. It is now found that, in these circumstances, a green fluorescence is produced which differs from that of fluorescein in being very transitory, and that subsequently the bluish-violet coloration of gallein becomes visible. The same intense but transitory fluorescence is produced when pyrogallol alone is heated with an excess of phthalic anhydride and the product dissolved in alkali; but simply warming the product with alcohol destroys the fluorescent substance and converts it into gallein. A similar fluorescence is obtained from pure gallein which has been fused with phthalic anhydride or with dicarboxylic acids which readily yield anhydrides on heating; that shown in the case of sebacic acid or diphenic acid is very intense and lasts several days.

W. A. D.

Tautomerism of the *o*-Aldehyde-acids. RUDOLF WEGSCHEIDER (*Ber.*, 1903, 36, 1541—1544).—Nitro-opianic acid has an extraordinarily small affinity constant, 0·00029, and is a very much weaker acid than opianic acid itself ($k = 0·0822$); it is suggested that its solution contains, principally, the *pseudo*-form,

$$NO_2·C_6H(OMe)_2<^{CH(OH)}_{CO\text{———}}>O.$$

From the silver salt of the acid and methyl iodide, a *methyl ester* is obtained which melts at 76—78° and is isomeric with Fink's methyl ester (*Ber.*, 1898, 31, 924); it is probably the *ψ-methyl ester.*

The very small affinity constant found in the case of this hydroxy-lactone makes it improbable that dicarboxylic acids, the constant of which exceeds 0·01, largely consist of a dihydroxy-lactonic form; in particular, Anschütz's view that maleic acid should be regarded as a dihydroxy-lactone is discounted.

W. A. D.

Chemical Action of Light. VI. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1903, 36, 1575—1583. Compare Abstr., 1901, i, 329, 390, 549; 1902, i, 433; this vol., i, 39, and 171).—When benzaldehyde is exposed to bright sunlight in a sealed vessel during the summer months, the chief products are a resinous substance, $(C_7H_6O)_9$, melting at 125—130°, and apparently a simple polymeride of the aldehyde, together with a resin soluble in alcohol and having the composition $C_{14}H_{14}O_2$.

Small amounts of benzoic acid and of unaltered benzaldehyde are also obtained. A mixture of benzaldehyde and benzyl alcohol, on exposure to sunlight, yields a mixture of hydrobenzoin, *iso*hydrobenzoin, resin, and the original substances.

Benzophenone and benzyl alcohol yield as chief product, benzopinacone, together with a substance, $C_{20}H_{18}O_2$, melting at 168°, hydrobenzoin, and a resin.

A solution of benzophenone in formic acid is not appreciably affected by light, whereas a solution of the same ketone in cymene yields benzopinacone. A benzaldehyde solution of benzophenone yields a small amount of a crystalline compound, $C_{41}H_{34}O_5$, crystallising in needles and melting at 236—237°.

An alcoholic solution of benzil yields at first crystals of benzilbenzoin; when kept, these redissolve, and ultimately resin, benzaldehyde, benzoic acid, ethyl benzoate, and benzoin are obtained.

Benzil and paracetaldehyde yield first crystals of benzilbenzoin, and ultimately a small amount of deoxybenzoin is formed.

Ethyl alcohol and opianic acid yield the *pseudo*-ester melting at 92°.

Alloxan and ethyl alcohol yield alloxantin and acetaldehyde.

When an aqueous solution of acetone is exposed to sunlight in sealed tubes, it yields acetic acid and methane according to the equation $COMe_2 + H_2O = MeCO_2H + CH_4$. If the vessel is not properly sealed, the products are formic and acetic acids. J. J. S.

Anils of the Methoxybenzaldehydes and their Behaviour with Methyl Iodide. MARTIN FREUND and FRANZ BECKER (*Ber.*, 1903, 36, 1537—1541).—o-*Methoxybenzylideneaniline*,

$$OMe\cdot C_6H_4\cdot CH\colon NPh,$$

obtained from *o*-methoxybenzaldehyde and aniline, is a viscid, reddish-yellow oil which boils at 235—236° under 30 mm. pressure; when heated with an excess of methyl iodide, a syrup is obtained which, on warming with dilute hydrochloric acid and subsequently distilling with steam, gives nearly equal quantities of *o*-methoxybenzaldehyde and salicylaldehyde. The methoxy-group has thus been largely converted into hydroxyl (compare this vol., i, 572).

m-*Methoxybenzylideneaniline* boils at 223—225° under 18 mm. pressure, and p-*methoxybenzylideneaniline* crystallises from alcohol in white needles and melts at 63°; by boiling with methyl iodide and subsequently treating the product with dilute acid, only traces of the hydroxy-aldehydes are obtained. In the case of *p*-methoxybenzylideneaniline, the only definite product is its *hydriodide*, $C_{14}H_{13}ON$, which crystallises from alcohol in sheaves of yellow needles and melts at 183—184°.

W. A. D.

Influence Exerted by the Introduction of Double Linkings into the Nuclei containing the Asymmetric Carbon Atom on the Rotatory Power of Cyclic Molecules. ALBIN HALLER (*Compt. rend.*, 1903, 136, 1222—1226).—Lists are given showing that the rotatory power of a substance (cyclic) is increased when a double linking is introduced.

Some derivatives of 3-methyl*cyclo*hexanone have been prepared and examined.

Benzylidene-3-methyl*cyclo*hexanone has $[\alpha]_D$ $-152°$ in alcoholic solution ($p = 0.2688$). *Anisylidene-3-methyl*cyclo*hexanone*,

$$C_5H_{10}<\begin{matrix}CO \\ | \\ C\colon CH\cdot C_6H_4\cdot OMe\end{matrix},$$

forms pale yellow, transparent prisms and melts at 97°; it has $[\alpha]$

$-225°$ (alcohol, $p = 0{\cdot}1053$). *Cuminylidene-3-methyl*cyclo*hexanone*, $C_5H_{10}<\begin{matrix}CO\\ |\\ C{:}CH{\cdot}C_6H_4{\cdot}Pr\end{matrix}$, forms pale yellow, transparent prisms and melts at 58°; it has $[\alpha]_D$ $-165°$ (alcohol, $p = 0{\cdot}3018$).

*Dianisylidene-3-methyl*cyclo*hexanone*, $C_4H_8<\begin{matrix}C({:}CH{\cdot}C_6H_4{\cdot}OMe)\\ C({:}CH{\cdot}C_6H_4{\cdot}OMe)\end{matrix}>CO$, forms yellow, transparent prisms and melts at 110°; it is insoluble in ether and in light petroleum.

*Dicuminylidene-3-methyl*cyclo*hexanone*, $C_4H_8<\begin{matrix}C({:}CH{\cdot}C_6H_4Pr)\\ C({:}CH{\cdot}C_6H_4Pr)\end{matrix}>CO$, is a viscid, oily liquid which boils at 300° under 10 mm. pressure. The disubstituted derivatives were too deeply coloured to be examined optically.

These derivatives were prepared from 3-methyl*cyclo*hexanone of $[\alpha]_D$ $-12°$ by the action of sodium methoxide and the appropriate aldehyde. It is evident that the introduction of an aromatic radicle by means of a double linking has caused an augmentation of the rotatory power.

The author suggests that the rotatory power is increased by the following circumstances: (1) by fixation by means of a single linking of unsaturated radicles on to an active nucleus; (2) by formation of a double linking in the nucleus without substitution or addition; (3) by attaching aliphatic or alicyclic radicles to the active nucleus by means of a double linking; (4) by a process of tautomerisation (from keto to enol); and (5) by combination of an active alcohol with an unsaturated acid. J. McC.

Preparation of Derivatives of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 139581).—The tertiary bases derived from aminoanthraquinone (this vol., i, 498), and still containing negative groups, are able, in spite of their strongly basic character, to react with aromatic amines. The colouring matters produced are red or violet when the substituents are in the 1 : 5- or 1 : 8-position, but are blue or green if these radicles are in the *p*-position.

1 : 5-*Methylamino*-p-*toluidinoanthraquinone*,

$$C_6H_4Me{\cdot}NH{\cdot}C_6H_3<\begin{matrix}CO\\ CO\end{matrix}>C_6H_3{\cdot}NHMe,$$

prepared by heating together *p*-toluidine and nitrodimethylaminoanthraquinone at 180°, crystallises from pyridine and methyl alcohol in long needles melting at 199°.

1 : 5-*Di*-p-*toluidino*-4 : 8-*dimethylaminoanthraquinone* dissolves in aniline, pyridine, chloroform, and acetic acid with a green colour, in hydrochloric acid with a violet colour.

When a dialkylated base is employed, one alkyl group is eliminated, and a monoalkylamino-derivative is obtained. C. H. D.

Migration of the Methyl Group in the Molecule of Camphor. GEORGES BLANC and MARCEL DESFONTAINES (*Compt. rend.*, 1903, 136, 1141—1143).—The experimental work already recorded (Abstr., 1902,

i, 299) on *d*-*a*-dihydrocampholenic acid and its derivatives has been repeated on the racemic forms. r-*Nitrocamphorimine*,

$$C_8H_{14}<\begin{matrix}C:N\cdot NO_2\\ | \\ CH_2\end{matrix},$$

melts at 28° and the *d*-form at 43°. *r*-*a*-Dihydrocampholenic acid and nitrile have the same boiling points as the *d*-forms; the corresponding racemic *amide* melts at 126°; the *d*-amide melts at 143°. r-*Dihydro-a-aminocampholene*, $NH_2\cdot CH_2\cdot CH<\begin{matrix}CMe_2\cdot CHMe\\ \quad\ | \\ CH_2-CH_2\end{matrix}$, boils, like the *d*-isomeride, at 190°, its *oxamide* melts at 150° (the *d*-form melts at 147—148°), the *picrate* melts and decomposes at 230° (the *d*-picrate melts at 227°), and the *racemic carbamide* at 112° (the *d*-carbamide melts at 119°).

r-4 : 5 : 5-*Trimethyl*cyclo*pentanone*, $CMe_2<\begin{matrix}CHMe\cdot CH_2\\ \quad\ | \\ CO\text{——}CH_2\end{matrix}$, boils at 164°, the *oxime* melts at 105° (the *d*-form melts at 188°); the *benzylidene* derivative is liquid, whilst that of the *d*-ketone is crystalline and melts at 34°. T. A. H.

Separation of *a*- and *β*-*cyclo*Citrals HAARMANN & REIMER (D.R.-P. 139957, 139958, and 139959. Compare Abstr., 1902, i, 385).—The condensation products of *β*-*cyclo*citral are more readily decomposed than those of *a*-*cyclo*citral. Advantage may be taken of this to separate the two isomerides. Thus, if a mixture of the *a*- and *β*-compounds is condensed with semicarbazide or aniline and distilled with steam in presence of a weak acid, only *β*-*cyclo*citral passes over.

a-cyclo*Citral* boils, when pure, at 90—95° under 20 mm. pressure, and has the sp. gr. 0·925—0·930. Its *semicarbazone* melts at 204—206°. *a*-*cyclo*Citral is also more stable towards reagents than *β*-*cyclo*citral. On shaking the crude mixture with dilute sodium hydroxide, *β*-*cyclo*-geranic acid is formed, *a*-*cyclo*citral remaining unaltered. By the action of sodium ethoxide and acetone on the crude *cyclo*citral below 0°, the *β*-compound is converted into *β*-ionone, the *a*-compound remaining unattacked.

a-*cyclo*Citral may be converted into *a*-ionone by the action of acetone in presence of strong alkalis. C. H. D.

Influence of the Double Linking between Carbon Atoms on the Rotatory Power of Optically Active Substances. HANS RUPE (*Annalen*, 1903, **327**, 157—200).—A *résumé* of the work on the influence of constitution on the rotatory power of optically active substances since 1896 is given in the introduction to this paper, the researches of Guye, Tschugaeff, and Frankland being especially considered.

[With ZELTNER.]—Although, according to Tschugaeff (Abstr., 1898, ii, 274), the menthyl esters of the fatty acids rotate the plane of polarised light to a less extent (5°) when dissolved in ethyl alcohol, a more extended investigation has shown there is no such regularity, the alcoholic solution in many cases exhibiting a greater specific rotatory power than the pure ester.

When an ethylene linking is present in the $\alpha\beta$-position, the rotatory power is greater than in the corresponding saturated acid; this increase is larger as the series is ascended from crotonic to pentenoic acid, but becomes less for members of the series above the acid last mentioned. When the ethylene linking is in the $\beta\gamma$-position, the rotatory power equals that of the unsaturated acid, whilst the $\alpha\delta$-unsaturated acid has a smaller rotatory power than the saturated acid. A conjugated system of ethylene linkings, as in menthyl sorbate, $CHMe⁚CH\cdot CH⁚CH\cdot CO_2\cdot C_{10}H_{19}$, produces a marked increase in the rotatory power.

The menthyl esters are prepared by treating the dry sodium salt of the acid with a solution of phosphorous oxychloride in benzene, and then adding a solution of menthol (1 mol.) in pyridine (2 mols.); esterification is complete after five to seven hours' boiling.

Menthyl crotonate, $CHMe⁚CH\cdot CO_2\cdot C_{10}H_{19}$, is a colourless oil boiling at 140—140·5° under 14 mm. pressure and has $[\alpha]_D$ −90·67°. *Menthyl $\Delta^{\alpha\beta}$-pentenoate*, $CH_2Me\cdot CH⁚CH\cdot CO_2\cdot C_{10}H_{19}$, boils at 152—153·5° and has $[\alpha]_D$ −74·41°. *Menthyl $\Delta^{\beta\gamma}$-pentenoate*, $CHMe⁚CH\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$, boils at 143—144·5° under 14 mm. pressure and has $[\alpha]_D$ −72·51°. *Menthyl $\Delta^{\gamma\delta}$-pentenoate* (*menthyl allylacetate*) boils at 139—140° under 14 mm. pressure and has $[\alpha]_D$ −67·32°. *Menthyl $\Delta^{\alpha\beta}$-hexenoate* boils at 163—164° under 14 mm. pressure and has $[\alpha]_D$ −68·38°. *Menthyl $\Delta^{\beta\gamma}$-hexenoate* boils at 149—150° under 14 mm. pressure and has $[\alpha]_D$ −65·11°. *Menthyl $\Delta^{\gamma\delta}$-hexenoate* boils at 156—157° and has $[\alpha]_D$ −60·93°. *Menthyl $\Delta^{\delta\epsilon}$-hexenoate* boils at 155—155·5° under 14 mm. pressure and has $[\alpha]_D$ −61·25°. *Menthyl $\Delta^{\alpha\beta}$-heptenoate* boils at 174—175·5° and has $[\alpha]_D$ −66·03°. *Menthyl sorbate* is a viscid oil boiling at 173° under 14 mm. pressure and has $[\alpha]_D$ −83·17° in benzene solution, whence, by calculation, $[\alpha]_D$ −88·53° in alcoholic solution.

The rotatory power of the cyclic menthyl esters of the cyclic acids, trimethylenecarboxylic acid, &c., is in general lower than those of the isomeric unsaturated open chain acids; the rotatory power of menthyl *cyclo*pentanecarboxylate is, however, very nearly equal to that of menthyl $\Delta^{\alpha\beta}$-hexenoate. *Menthyl trimethylenecarboxylate* is a colourless oil boiling at 135—135·5° under 14 mm. pressure and has $[\alpha]_D$ −68·53° in alcoholic solution; *menthyl tetramethylenecarboxylate* boils at 148° under 14 mm. pressure and has $[\alpha]_D$ −69·09°.

[With Walther Lotz.]—*Menthyl pentamethylenecarboxylate* boils at 160·5—161° under 14 mm. pressure and has $[\alpha]_D$ −67·94°. *Menthyl* cyclo*hexanecarboxylate* (*hexahydrobenzoate*) crystallises in white needles melting at 48°, boils at 166° under 8 mm. or at 170° under 12 mm. pressure, and has $[\alpha]_D$ −59·11°.

The effect of reducing the menthyl esters of benzoic acid and α-naphthoic acid is best shown in the following table:

Menthyl ester of	$[\alpha]_D$.	Difference from benzoic acid.
Benzoic acid	−83·53	
Δ^1-Tetrahydrobenzoic acid	−74·64	8·39°
Hexahydrobenzoic acid	−59·11	24·42

Menthyl ester of	$[\alpha]_D$.	Difference from α-naphthoic acid.
α-Naphthoic acid	−79·08°	
Δ^1-Dihydro-α-naphthoic acid	−69·12	9·96°
Tetrahydro-α-naphthoic acid	−47·57	31·51

Menthyl Δ^2-tetrahydrobenzoate behaves as a $\beta\gamma$-unsaturated acid, thus:

Menthyl ester of	$[\alpha]_D$.	Difference.	Menthyl ester of	$[\alpha]_D$.	Difference.
Benzoic acid........	−83·53°		Sorbic acid	−88·53°	
		24·09°			23·42
Δ^2-Tetrahydrobenzoic acid	−59·44		$\beta\gamma$-Hexenoic acid ...	−65·11	
		0·33			0·25
Hexahydrobenzoic acid	−59·11		Hexoic acid	−64·86	

[With Max Silberberg.]—*Menthyl benzoate*, prepared from benzoyl chloride and menthol, melts at 55° and boils at 177° under 11 mm. pressure; *menthyl* Δ^1-*tetrahydrobenzoate* boils at 176° under 10 mm. pressure; *menthyl* Δ^2-*tetrahydrobenzoate* boils at 176° under 12 mm. pressure; *menthyl a-naphthoate* is a gum boiling at 231—232° under 11 mm. pressure; *menthyl* Δ^1-*dihydro-a-naphthoate* is a gum boiling at 226—227·5° under 12 mm. pressure. *Menthyl* Δ^2-*dihydro-a-naphthoate* crystallises in colourless prisms melting at 89—89·5°; it is dextrorotatory, having $[\alpha]_D$ +92·85° in solution in ethyl acetate; this peculiarity in the optical activity is not due to a change in the menthol but to the presence of an asymmetric carbon atom in the dihydronaphthoic acid. *Menthyl tetrahydro-a-naphthoate* is a very viscous liquid boiling at 207° under 10 mm. pressure. K. J. P. O.

Terpenes and Ethereal Oils. Pulegenic Acid and its Derivatives. Otto Wallach (*Annalen*, 1903, 327, 125—157. Compare Abstr., 1896, i, 309; 1898, i, 484)—[With Julius Meyer and Fritz Collmann].—Pulegenic acid is best prepared by boiling pulegone dibromide with excess of sodium methoxide dissolved in anhydrous methyl alcohol; when quite pure, it remains colourless and does not decompose on keeping. Its methyl ester (*loc. cit.*) is readily prepared by treating its solution in methyl alcohol with sulphuric acid; it boils at 114—115° under 30 mm. pressure and can only be hydrolysed by alkalis with great difficulty. On oxidising the ester (3 mols.) with permanganate (2 mols.), a dihydroxy-ester,

$$C_9H_{15}(OH)_2{\cdot}CO_2Me,$$

is formed; it melts at 118—119°, and is hydrolysed extremely easily, yielding dihydroxypulegenic acid, which, however, immediately loses water, giving the hydroxy-lactone (m. p. 129—130°) previously described (*loc. cit.*). The dihydroxy-ester yields a *benzoyl* derivative, $C_9H_{15}(OBz)_2{\cdot}CO_2Me$, melting at 204—206°. Pulegenic chloride is readily prepared and when treated with concentrated ammonia yields the amide melting at 121—122° and the *anilide* melting at 124°.

The lactone, $C_{10}H_{16}O_2$, of pulegenic acid can be easily prepared by boiling the acid with 25 per cent. sulphuric acid, and is freed from other substances by treatment with one per cent. permanganate, which has no action on the lactone, whilst it oxidises the impurities; it melts at 30—31° and boils at 126—128° under 12 mm. pressure (compare *loc. cit.*); it is identical with the compound obtained by boiling the additive product of hydrogen bromide and pulegenic acid with alcoholic potassium hydroxide, and with that prepared by the decomposition of the additive product of hydrogen chloride and ethyl pulegenate.

[With Fritz Collman and Joh. Thede.]—Pulegene, prepared by heating pulegenic acid in hydrogen at 180—200°, readily yields a *nitrosochloride*, $C_9H_{16}{\cdot}NOCl$, when a solution of the hydrocarbon together with amyl nitrite is treated with a solution of hydrogen chloride in acetic acid; it melts at 74—75°. *Pulegennitrolpiperidide*, $C_9H_{16}{\cdot}NO{\cdot}C_5NH_{10}$, prepared from the nitrosochloride and piperidine, melts at 106—107°.

Pulegenone-oxime, $C_9H_{14}{:}N{\cdot}OH$, is prepared by warming the nitrosochloride with sodium methoxide dissolved in methyl alcohol at 30—40°; it is an oil boiling at 123—126° under 15 mm. and at 237—242° under the ordinary pressure; its *benzoyl* derivative melts at 104—105°. From the oxime, pulegenone is obtained by heating with dilute sulphuric acid; the ketone is then converted into its *semicarbazone*, which melts at 183—184° and is easily hydrolysed by dilute sulphuric acid, giving pulegenone in a pure state; it boils at 189—190°, has a sp. gr. 0·914, and n_D 1·4645 at 20°. On oxidation with permanganate, *iso*butyric acid was obtained. When reduced by sodium in ethereal or alcoholic solution, pulegenone is converted into *pulegenol*, $C_9H_{17}{\cdot}OH$, boiling at 77—78° under 15 mm. pressure; with phenylcarbimide, it yields the *phenylurethane*, $C_9H_{17}{\cdot}O{\cdot}CO{\cdot}NHPh$, which crystallises in needles melting at 81—82°.

Dihydropulegenone, $C_9H_{16}O$, is prepared by oxidising dihydropulegenol with chromic acid; it boils at 184—185°, and has a sp. gr. 0·8875 and n_D 1·440 at 20°; its *semicarbazone* melts at 193—195° and at 198—199° when rapidly heated, and is easily converted into the ketone by warming with dilute sulphuric acid; the *oxime* melts at 77—78°. Attention is drawn to the fact that pulegenone and dihydropulegenone are quite distinct from the isomeric ketones obtained from *cyclo*geraniolene. On oxidising dihydropulegenone (1 mol.) with permanganate (2 mols.), a mixture of acids is obtained from the semicarbazones, of which two isomeric semicarbazones could be isolated, one, melting at 164°, identical with the compound obtained by oxidising pulegene (see below), and a second melting at 140—143° (?). The latter yields, on treatment with sulphuric acid, a ketonic acid, $C_9H_{16}O$, which boils at 154—155° under 15 mm. pressure, and is oxidised by hypobromite to bromoform or carbon tetrabromide and an *acid*, $C_6H_{12}(CO_2H)_2$; this compound melts at 94—95° and gives an insoluble *silver* salt, $C_6H_{12}(CO_2Ag)_2$; it is probably the hitherto unknown α-iso*propylglutaric acid.*

[With Eugen Seldis.]—On oxidising pulegene with permanganate, a ketonic acid is formed, together with acetic acid; the former is purified by conversion into its *semicarbazone*, which forms prismatic crystals melting at 164°; the acid itself, $C_8H_{15}O{\cdot}CO_2H$, prepared from the semicarbazone, is a yellow oil boiling at 164° under 15 mm. pressure; its *silver* salt was analysed; the *oxime*, $C_8H_{15}(NOH){\cdot}CO_2H$, of this acid melted at 76—77°. When oxidised with hypobromite, a mixture of two acids was formed, from which methylsuccinic acid (m. p. 110°) was isolated; the other acid was probably α-methylglutaric acid (m. p. 79°), which was obtained in quantity together with acetone when the ketonic acid was oxidised by chromic acid. The ketonic acid was compared and found to be identical with the acid of the same composition

prepared by Tiemann and Semmler (Abstr., 1898, i, 629) by oxidising carvenone with permanganate.

A consideration of the various transformations which may occur when pulegone dibromide, $CHMe<{CH_2\cdot CH_2 \atop CH_2-CO}>CHBr\cdot CBrMe_2$, is converted into pulegenic acid, and the fact that this acid so readily yields a lactone, and, by loss of carbon dioxide, a hydrocarbon, pulegene, which is not identical with *cyclo*geraniolene, lead to the conclusion that pulegenic acid has a five-membered ring, and is most probably represented by the expression ${CH_2-CHMe \atop CH_2\cdot C(:CMe_2)}>CH\cdot CO_2H$. The reactions of pulegene point to a change in the position of the double linking in the conversion of the acid into the hydrocarbon, which most probably has the formula ${CHMe\cdot CH \atop CH_2-CH_2}>CPr^{\beta}$. The nitrosochloride then has the formula

$${CHMe\cdot C(:NOH) \atop CH_2\text{———}CH_2}>CClPr^{\beta},$$

the oxime the formula ${CHMe\cdot C(:NOH) \atop CH_2\text{———}CH}\geqslant CPr^{\beta}$, and pulegenone the formula ${CHMe\cdot CO \atop CH_2-CH}\geqslant CPr^{\beta}$; hence dihydropulegenone is 1-methyl-3-*iso*propyl-2-pentanone. Pulegenone is then isomeric with Semmler's camphorphorone (Abstr., 1902, i, 385), and dihydrocamphorphorone must be identical with dihydropulegenone. A comparison of their properties (melting point, sp. gr., and n_D, and characters of semicarbazone) entirely confirms this supposition. K. J. P. O.

Ethereal Oils. SCHIMMEL and Co. (*Chem. Centr.*, 1903, i, 1086—1087; from Schimmel's *Geschäftsber*, April, 1903).—Samples of oil of amber have been prepared which had a sp. gr. 0·9259—0·9295 at 15°, rotatory power +22°32′ to +26°, n_D 1·50802—1·51083 at 20°, acid number, 5·1—6·5, and ester number, 3·85—8·95, and were soluble in 4—4·5 volumes of 95 per cent. alcohol.

The lævorotatory form of citronellal has been isolated together with cineol from an oil of citronella obtained from Java.

A sample of lavender oil which had a sp. gr. 0·8902 at 15°, rotatory power −7°6′, and saponification number 116·5 = 40·7 per cent. of linalyl acetate, was found to contain valeraldehyde (?), amyl alcohol, pinene, cineol (eucalyptol), *d*-borneol, geraniol, geraniol acetate and capronate, coumarin, and about 0·2 per cent. of a ketone, $C_8H_{16}O$, which is probably identical with ethyl amyl ketone. Methyl heptyl ketone, boiling at 191—196°, has been detected in oil of cloves (compare Abstr., 1902, i, 550). The semicarbazone prepared from the artificial or the natural ketone melts at 118—119°. Contrary to Hesse and Zeitschel's statement (this vol., i, 189), the Neroli oil examined by Semmler and Tiemann was a genuine oil. Further examination has shown that the oil contains phenylethyl alcohol and, probably, jasmone (compare Hesse, Abstr., 1900, i, 48). Attempts to purify nerol

isolated from neroli oil by Hesse and Zeitschel (*loc. cit.*), and from oil of petit grain by von Soden and Zeitschel (this vol., i, 267) did not yield definite results.

The cohobation water of sade-wood oil and the distillation water of West Indian sandal-wood oil contained diacetyl, furfuraldehyde, and methyl alcohol. Attempts to isolate tuberone (Verley, Abstr., 1899, i, 712) from the blue fluorescent oil obtained by distilling tuberose extract failed. When the fraction boiling at 60—140° under 5 mm. pressure was oxidised by potassium permanganate, benzoic acid was formed, together with an oil. The latter was not further attacked by permanganate, and on hydrolysis gave a product which contained benzoic acid and had an odour similar to that of methyl benzoate.

In addition to the compounds already detected in Ylang-Ylang oil the presence has been proved of pinene, creosol, eugenol, *iso*eugenol, eugenol methyl ether, benzyl alcohol, benzyl acetate, benzyl benzoate, methyl benzoate, methyl salicylate, methyl anthranilate, and an odourless sesquiterpene alcohol melting at 138°.

A wood from the Botanical Garden at Amani, in German East Africa, was found to be covered with lustrous crystals of scatole (compare Dunstan, Abstr., 1890, 191).

An appendix to the original paper contains the results of an investigation made by Hans Kleist of the physiological action of anthranilic acid, methyl acetylanthranilate, methyl methylanthranilate, methyl acetylmethylanthranilate, and piperonal (heliotropine) on warm- and cold-blooded animals. E. W. W.

Sugars of Jalapin and other Vegetable Glucosides. Emil Votoček and R. Vondráček (*Zeit. Zuckerind. Böhm.*, 1903, 27, 257—271, and 333—340).—On hydrolysis, naringin yields the two sugars, dextrose and rhamnose, the latter constituting 48·23 per cent. of the reducing sugars formed.

Jalapin gives dextrose, rhodeose, and possibly, also, *iso*rhodeose.

Solanin yields rhamnose and a hexose which gives a phenylmethylhydrazone crystallising in colourless leaflets melting at 187°; this indicates the presence of a new hexose, either with or without dextrose.

Convalarin gives a sugar which yields a white powder, probably mucic acid, on oxidation with nitric acid, indicating the presence of galactose.

Convallamarin yields a sugar syrup having the specific rotation $[\alpha]_D$ +48°, and containing a hexose probably identical with that of solanin, galactose (?), and a methylpentose. It is uncertain whether the galactose obtained has its origin in the glucoside or in admixed galactan.

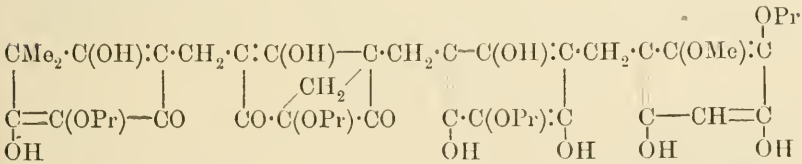
These results show that methylpentoses are much more widely distributed in the vegetable kingdom than has been hitherto assumed; such sugars are also probably contained in convalarin and smilacin.

T. H. P.

Filmarone, the Active Constituent of Filix Extract. FRIEDRICH KRAFT (*Chem. Centr.*, 1903, i, 1090; from *Pharm. Zeit.*, 48, 275—276).—Filmarone, $C_{47}H_{54}O_{16}$, the amorphous substance contained in Filix extract (Abstr., 1902, i, 814), is the cause of the anthelmintic action of the extract. It is stable in the dry state or in solvents such as benzene, carbon disulphide, ether, &c., but is slowly decomposed by the action of acetone or of mixtures of alcohol and ether. When the acetone solution is allowed to remain for a long time, filicic acid and amorphous filicinigrin are formed. By the simultaneous action of boiling alkalis and nascent hydrogen, filmarone yields filicic acid and aspidinol or the decomposition products of these substances. By the action of diazoaminobenzene on filmarone, the azo-compound characteristic of filicic acid and flavaspidic acid is formed.

The results of pharmacological and therapeutic tests made by Jaquet show that filmarone may be used instead of the extract. In doses of 0·5—0·7 gram, the action is the same as that of the extract, and is not accompanied by other injurious effects.

The constitution



is assigned to filmarone. E. W. W.

Binaphthylenethiophen and Trinaphthylenebenzene. PAUL REHLÄNDER (*Ber.*, 1903, 36, 1583—1587. Compare Dziewónski, this vol., i, 431).—The compounds described by Dziewónski have been previously prepared by the author (*Inaug. Diss.*, 1903) by very similar methods. The crude mass was extracted with xylene to remove the thiophen. Trinaphthylenebenzene is not oxidised when boiled with acetic acid and sodium dichromate. J. J. S.

Apocodeine and Piperidinocodide. EDUARD VONGERICHTEN and FRITZ MÜLLER (*Ber.*, 1903, 36, 1590—1594).—Apocodeine (Göhlich Abstr., 1893, i, 676) is not a true analogue of apomorphine (this vol., i, 193) since it contains no phenolic hydroxyl group and does not yield a product corresponding with methylmorphimethine when its methiodide is decomposed.

A resinous base is produced when chlorocodide (Abstr., 1882, 311) is reduced with sodium methoxide and methyl alcohol at 100°. Its *hydrochloride*, $C_{18}H_{19}O_2N,HCl$, is an oil, which, on treatment with bromobenzoyl chloride in ethereal solution and alkali, yields a base, the *hydrochloride*, $C_6H_4Br\cdot CO\cdot C_{18}H_{18}O_2N,HCl$, of which is a colourless hygroscopic substance. *Piperidinocodide*, $C_{23}H_{30}O_2N_2$, obtained by the action of piperidine on chlorocodide, crystallises from methyl alcohol in long, colourless prisms containing MeOH. It begins to sinter at 60° and melts about 116°; when dried at 100°, it melts at

118°. The base is readily soluble in alcohol, but insoluble in water, its *hydrochloride*, $C_{23}H_{30}O_2N_2,2HCl$, is a white, hygroscopic compound readily soluble in water to a neutral solution. The *monomethiodide*, $C_{23}H_{30}O_2N_2,MeI$, forms colourless crystals melting at 256° and only sparingly soluble in water or alcohol. The *dimethiodide* melts at about 250°. The monomethiodide reacts with sodium hydroxide in very much the same manner as codeine methiodide, the nitrogen ring is ruptured, and a tertiary base, *piperidino-methylmorphimethine*,

$$C_{24}H_{32}O_2N_2,$$

is obtained as a colourless oil. With acetic anhydride at 180°, it yields a yellow, non-basic oil not identical with acetylmethylmorphol; with methyl iodide, it yields a *monomethiodide*, $C_{24}H_{32}O_2N_2,MeI$, melting at 248°, and a *dimethiodide* in the form of a resin fairly readily soluble in water.

When treated with alcoholic potash, the piperidino-methylmorphinmethine methiodide yields a phenolic substance not identical with morphenol. J. J. S.

Cotarnine. MARTIN FREUND and FRANZ BECKER (*Ber.*, 1903, 36, 1521—1537).—By the following considerations, the relative position of the methoxyl radicle and the $CH_2{:}O_2{:}$ group in cotarnine is determined, and the structure of the alkaloid shown to be

$$CH_2<\begin{matrix}O\cdot C{:}C(OMe)\cdot C\cdot CHO\\ O\cdot C{:}CH \text{———} C\cdot CH_2\cdot CH_2\cdot NHMe\end{matrix};$$

whence also the structure of narcotine is

$$CH_2<\begin{matrix}O\cdot C{:}C(OMe)\cdot C \text{————} CH \text{—} CH \text{—} C{:}CH\cdot CH\\ O\cdot C{:}CH \text{——} C\cdot CH_2\cdot CH_2\cdot NMe \quad O\cdot CO\cdot C{:}C(OMe)\end{matrix}>C\cdot OMe.$$

Cotarnineanil, $CH_2<{O \atop O}>C_6H(OMe)<{CH{:}NHPh \atop CH_2\cdot CH_2\cdot NHMe}$, combines with methyl iodide, forming cotarninemethine methiodide anil, $CH_2<{O \atop O}>C_6H(OMe)<{CH{:}NHPh \atop CH_2\cdot CH_2\cdot NMe_3I}$, which, by an excess of methyl iodide and subsequent warming with dilute acid, is converted into norcotarninemethine methiodide, $CH_2<{O \atop O}>C_6H(OH)<{CHO \atop CH_2\cdot CH_2\cdot NMe_3I}$. As such a displacement of the methyl of a methoxyl group by hydrogen takes place only in the case of *o*-methoxyaldehydes (this vol., i, 563), and not in the case of compounds containing methoxyl and CHO in the meta- or para-position relatively to each other, the position occupied by these groups in cotarnine is established. The displacement of the methyl radicle probably occurs in the following manner:

$$\text{I.}\quad CH_2<\begin{matrix}O\cdot C\cdot C(OMe){:}C\cdot CH{:}NPh\\ O\cdot C\cdot CH{=\!=}C\cdot CH_2\cdot CH_2\cdot NMe_3I\end{matrix} \longrightarrow$$

$$\longrightarrow CH_2<\begin{matrix}O\cdot C\cdot C(OMe){:}C\cdot CH{:}NMePhI\\ O\cdot C\cdot CH{=\!=}C\cdot CH_2\cdot CH_2\cdot NMe_3I\end{matrix} \longrightarrow$$

$$\longrightarrow CH_2<\begin{matrix}O\ C\cdot C{=\!=}C\cdot CH{:}NMePh\\ O\cdot C\cdot CH{=}C\cdot CH_2\cdot CH_2\cdot NMe_3I\end{matrix} \longrightarrow$$

$$\longrightarrow CH_2<\begin{matrix}O\cdot C\cdot C(OH){:}C\cdot CHO\\ O\cdot C\cdot CH{=\!=}C\cdot CH_2\cdot CH_2\cdot NMe_3I\end{matrix} + NHMePh.$$

This elimination of methylaniline was experimentally established.

Cotarnineanil, prepared directly from its constituents, crystallises from ether, alcohol, or benzene in slender needles and melts at 124°; *cotarnine*-p-*ethoxyanil*, prepared from cotarnine and *p*-phenetidine, crystallises from alcohol and melts at 120°; *ethyl cotarnineanil*-p-*carboxylate*, prepared by using *p*-aminobenzoic acid, forms white needles and melts at 147°.

Cotarninemethine methiodide anil (*supra*), crystallises from water in yellow needles and melts at 199°. *Norcotarninemethine methiodide* crystallises from dilute alcohol in yellow needles, melts at 272°, and on methylation with methyl iodide and sodium ethoxide is reconverted into cotarninemethine methiodide; when boiled with 30 per cent. aqueous sodium hydroxide, it evolves trimethylamine and is converted into *norcotarnone*, $CHO{\cdot}C_6H(OH)(O_2CH_2){\cdot}CH{:}CH_2$, which separates from alcohol in yellowish-green crystals, melts at 89°, and gives a golden-yellow, crystalline *potassium* salt. The *triacetyl* derivative, $CH(OAc)_2{\cdot}C_6H(OAc)(O_2CH_2){\cdot}CH{:}CH_2$, prepared by heating norcotarnone with acetic anhydride and sodium acetate, crystallises from acetone on adding light petroleum in prisms and melts at 124°. The *oxime*, $OH{\cdot}N{:}CH{\cdot}C_6H(OH)(O_2CH_2){\cdot}CH{:}CH_2$, crystallises from alcohol in leaflets, melts at 202—203°, and when dissolved in acetic anhydride gives the *acetate*, $OAc{\cdot}N{:}CH{\cdot}C_6H(OH)(O_2CH_2){\cdot}CH{:}CH_2$, which crystallises from alcohol in silken needles, melts at 130°, and is converted by warm sodium carbonate solution into *norcotarnonitrile*, $CN{\cdot}C_6H(OH)(O_2CH_2){\cdot}CH{:}CH_2$; this separates from glacial acetic acid or alcohol in needles, melts at 202°, and gives a crystalline *sodium* salt with H_2O, and an *acetyl* derivative,

$$CN{\cdot}C_6H(OAc)(O_2CH_2){\cdot}CH{:}CH_2,$$

crystallising in lustrous needles and melting at 110°. *Acetylnorcotarnone*, $CHO{\cdot}C_6H(OAc)(O_2CH_2){\cdot}CH{:}CH_2$, obtained from the sodium salt of norcotarnone and cold acetic anhydride, crystallises from glacial acetic acid or alcohol in lustrous needles and melts at 84—85°; its *oxime*, $OH{\cdot}N{:}CH{\cdot}C_6H(OAc)(O_2CH_2){\cdot}CH{:}CH_2$, crystallises from alcohol, melts at 115—116°, and, like its isomeride, on heating with alkalis yields norcotarnonitrile; the *diacetyl* derivative,

$$OAc{\cdot}N{:}CH{\cdot}C_6H(OAc)(O_2CH_2){\cdot}CH{:}CH_2,$$

melts at 100—101°.

The following analogous derivatives of bromocotarnine,

$$CHO{\cdot}C_6Br(OMe)(O_2CH_2){\cdot}CH_2{:}CH_2{\cdot}NHMe,$$

were prepared; the *anil*, $C_{18}H_{19}O_3N_2Br$, crystallises from ether in slender, white needles and melts at 127°. *Bromonorcotarninemethine methiodide*, $C_{13}H_{17}O_4NBrI$, crystallises from water in slightly yellow needles and decomposes at 264°. *Bromonorcotarnone* crystallises from alcohol in greyish-white needles, melts at 138°, and gives a *sodium* salt crystallising in lustrous, yellow spangles with $3\frac{1}{2}H_2O$.

Benzoylcotarnineanil, $NPh{:}CH{\cdot}C_6H(OMe)(O_2CH_2){\cdot}CH_2{\cdot}CH_2{\cdot}NMeBz$, crystallises from alcohol in needles, melts at 165°, and is not changed when boiled with methyl iodide; when heated with the latter at 100°, a complex decomposition occurs. W. A. D.

Mixed Carbamides of Piperidine and Aromatic Amines. Bouchetal de la Roche (*Bull. Soc. chim.*, 1903, iii, 29, 409—411).—When a symmetrical carbamide is warmed in a closed tube at 170° with a large excess of piperidine, there is formed a mixed carbamide containing a piperidine residue; thus, when diphenylcarbamide is so treated, *phenylpiperidinecarbamide*, $C_5H_{10}N\cdot CO\cdot NHPh$, is produced; this forms small, colourless crystals and melts at 168°. o-*Tolylpiperidinecarbamide*, $C_5H_{10}N\cdot CO\cdot NH\cdot C_6H_4Me$, similarly prepared, melts at 143°, the corresponding p-*tolyl* compound melts at 143°, and the p-*nitrophenylpiperidinecarbamide* at 157°.

These mixed carbamides are not produced by the action of aromatic amines on the piperidinecarbamates (Abstr., 1902, i, 562).

T. A. H.

Condensation of aa'-Lutidine [2:6-Dimethylpyridine] with Aldehydes. Fritz Werner (*Ber.*, 1903, 36, 1683—1689).—p-*Methylbenzylidene-aa'-lutidine* [*2-styryl-6-methylpyridine*],

$$C_5NH_3Me\cdot CH\colon CH\cdot C_6H_4Me,$$

prepared from 2:6-dimethylpyridine and *p*-tolualdehyde, crystallises from dilute alcohol in white, pearly flakes and melts at 144—145°. The *hydrochloride* is too soluble to be readily purified. The *aurichloride*, $C_{15}H_{15}N,HAuCl_4$, forms long, red needles and melts at 210—211°. The *mercurichloride*, $C_{15}H_{15}N,HCl,HgCl_2$, separates from dilute hydrochloric acid in clear, yellow crystals and melts at 195°. The *platinichloride*, $(C_{15}H_{15}N)_2,H_2PtCl_6$, separates from dilute hydrochloric acid in reddish-yellow needles which blacken at 220° and do not melt at 260°. The *picrate* separates from alcohol, in which it is very sparingly soluble, in glistening flakes, and melts and decomposes at 226°. The *dibromide*, $C_{15}H_{15}NBr_2$, darkens at 144° and melts at 154°.

Bis-p-*methylbenzylidene-aa'-lutidine* [2:6-*distyrylpyridine*],

$$C_5NH_3(CH\colon CH\cdot C_6H_4Me)_2,$$

formed as a bye-product in the preparation of the preceding base, separates from boiling alcohol (a litre of which is required to dissolve 3 grams) in nacreous flakes and melts at 202°. The *hydrochloride*, $C_{23}H_{21}N,HCl,H_2O$, crystallises in yellow needles from very dilute alcohol, sinters at 196°, and melts and decomposes at 215°. The *hydrobromide*, $C_{23}H_{21}N,HBr,H_2O$, forms beautiful, yellow needles, sinters at 265°, and melts at 272°. The *aurichloride*, $C_{23}H_{21}N,HAuCl_4$, separates from dilute alcohol in reddish-yellow needles and melts at 177°. The *mercurichloride*, $C_{23}H_{21}N,HCl,HgCl_2$, crystallises from dilute alcohol in yellowish-green needles, which begin to decompose at 146° and melt at 231°. The *platinichloride*, $(C_{23}H_{21}N)_2,H_2PtCl_6$, separates from dilute alcohol in yellow needles, begins to decompose at 220°, and melts at 236°. The *picrate* crystallises from alcohol in well-defined, yellow needles and melts at 226°. The *tetrabromide*, $C_{23}H_{21}NBr_4$, crystallises from dilute acetic acid in small needles and melts at 182°.

m-*Nitrophenyl-aa'-lutidylalkine* [2-m-*nitro-a-hydroxydihydrostyryl*-6-*methylpyridine*], $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot C_5H_3NMe$, prepared from *m*-nitrobenzaldehyde and 2:6-dimethylpyridine, separates from alcohol in small, white needles with $1H_2O$ and melts in its water of crystallisation at 82—83°; the anhydrous base melts at 96°. The

hydrochloride, $C_{14}H_{14}O_3N_2,HCl$, separates from dilute hydrochloric acid, in which it is readily soluble, in white needles, and melts at 205°. The *picrate* crystallises from dilute alcohol in minute flakes and melts at 139—140°. The *mercurichloride*, $C_{14}H_{14}O_3N_2,HCl,HgCl_2$, separates from dilute alcohol in warty needles and melts at 199°. The *platinichloride*, $(C_{14}H_{14}O_3N_2)_2,H_2PtCl_6$, forms reddish-yellow needles and melts at 208° with vigorous liberation of gas.

2 : 6-*Di*-p-*nitrostyrylpyridine*, $C_5NH_3(CH{:}CH{\cdot}C_6H_4{\cdot}NO_2)_2$, prepared from *p*-nitrobenzaldehyde and 2 : 6-dimethylpyridine, crystallises from slightly dilute alcohol in yellow flakes and melts at 168—169°. The *hydrochloride*, $C_{21}H_{15}O_4N_3,HCl,H_2O$, forms long, yellow needles, begins to darken at 220°, and melts and decomposes at 263°. The *platinichloride*, $(C_{21}H_{15}O_4N_3)_2,H_2PtCl_6$, separates from dilute alcohol in reddish-yellow needles and begins to decompose at 250°, but does not melt at 270°. The *mercurichloride*, $C_{21}H_{15}O_4N_3,HCl,HgCl_2$, separates from alcohol in small needles, begins to darken at 240°, and melts at 275°. The *aurichloride*, $C_{21}H_{15}O_4N_3,HAuCl_4$, separates from alcohol in small, golden-yellow needles, darkens at 208°, and melts at 233°. The *picrate* separates from alcohol in small needles and melts at 246°. The *tetrabromide*, $C_{21}H_{15}O_4N_3Br_4$, crystallises from hot alcohol and melts at 252° to a dark brown liquid. The *amino*-base, $C_{21}H_{19}N_3$, crystallises from dilute alcohol and melts at 146°; its *platinichloride*, $(C_{21}H_{19}N_3)_2,H_2PtCl_6$, crystallises from very dilute alcohol in small, reddish-brown needles, becomes brown at 250°, and does not melt at 275°; the *mercurichloride*, $C_{21}H_{19}N_3,HCl,HgCl_2$, crystallises from dilute alcohol in yellow needles, blackens at 220°, and melts at 243°.

T. M. L.

Preparation of 2 : 6-Diphenylpyridine-3-carboxylic Acid. TIMOTHÉE KLOBB (*Bull. Soc. chim.*, 1903, [iii], 29, 407—409).—When methyl or ethyl cyanodiphenacylacetate (Abstr., 1897, i, 531) is heated with potassium hydroxide dissolved in alcohol, there is formed, when air is freely admitted, the cinnabar-red compound, $C_{18}H_{15}O_3N$, already described (*loc. cit.*), and in the presence of air the 2 : 6-diphenylpyridine-3-carboxylic acid, prepared by Paal and Strasser (Abstr., 1888, 62). This acid crystallises in compact masses of colourless needles, melts at 278—279°, and sublimes unchanged. The *potassium* salt, precipitated from its aqueous solutions by addition of potassium carbonate, crystallises in long needles; the *sodium* salt forms hexagonal lamellæ, and the *silver* salt is a white powder which does not blacken at 100°; on ignition, it leaves a residue of silver carbide and cannot therefore be used to identify the acid.

T. A. H.

Partial Racemism. ALBERT LADENBURG and O. BOBERTAG (*Ber.*, 1903, 36, 1649—1652).—In view of the controversy respecting the existence of partial racemism (for references, see Trans., 1899, 75, 466), the authors have again examined β-pipecoline hydrogen tartrate, in which this phenomenon was first observed (Abstr., 1894, i, 208). On evaporating a solution of this salt at 50° and decomposing with potassium hydroxide, an inactive base is obtained, whilst the base obtained from a solution evaporated at 35° is slightly lævorotatory.

r-β-Pipecoline hydrogen tartrate is anhydrous, the *l*- and *d*-forms

crystallise with 1 mol. and ½ mol. H_2O respectively. The principal properties of the salts are as follows:

Form.	Melting point.	Sp. gr. Cryst.	Sp. gr. Dehydrated.
r-	144—146°	—	1·285
l-	170—172	1·271	1·219
d-	76— 78	1·420	1·318

The racemic salt can be reproduced by mixing molecular proportions of the *l*- and *d*-forms and evaporating on the water-bath.

The transition-point was determined by a comparison of the vapour pressure of a saturated solution of the *r*-salt in water with that of the hydrated crystals of the mixture of *l*- and *d*-salts in a Bremer-Frowein differential tensimeter, and was found to lie at 39°. This was confirmed by measurements of the solubility in alcohol at this temperature. C. H. D.

Pyrophthalone and its Derivatives. Hermann von Huber (*Ber.*, 1903, 36, i, 1653—1666).—The constitution of pyrophthalone is usually represented, from analogy with the quinophthalones studied by Eibner (compare Abstr., 1901, i, 348, 611), by the second of the two possible formulæ:

I. $C_6H_4<\substack{CO \\ CO}>CH{:}C_5NH_4$ and II. $C_6H_4<\substack{CO \\ -O-}>C{:}CH{\cdot}C_5NH_4$.

The author has investigated the question more fully, and has also prepared the isomeric form indicated by theory.

Pyrophthalone is most easily prepared by heating together pure α-picoline and phthalic anhydride in mol. proportions with a little zinc chloride on an oil-bath at 200°. The product melts at 260°. On reduction with zinc dust and acetic acid, an uncrystallisable oil, boiling at 140—160° under 10 mm. pressure, is obtained. The constitution was determined by the analysis of the salts to be that of a secondary alcohol. The *hydrochloride*, $C_{14}H_{13}ON,HCl$, forms white needles melting at 72°. The *nitrate*, long, colourless needles melting at 135°, the *platinichloride*, brownish-yellow needles melting at 175°, the *aurichloride*, bright yellow needles melting at 146—147°, and the *mercurichloride*, white needles melting at 172°. The *picrate*, golden-yellow needles melting at 126°, the *methiodide*, dark red needles melting at 130°. The *benzoate* crystallises from ether in small, white needles which melt at 36—37°.

iso*Pyrophthalone* may be prepared by heating phthalic anhydride with an excess of α-picoline in a sealed tube at 230°. After removal of picoline by hydrochloric acid, the product is crystallised from acetic acid and alcohol and separates in large, orange-yellow leaflets melting at 280°. The same compound is obtained when α-picoline reacts with phthalyl chloride in benzene solution. This synthesis determines the asymmetrical constitution of *iso*pyrophthalone, and pyrophthalone must therefore have the symmetrical constitution (I).

An intermediate product, containing chlorine, could be isolated in the form of its *hydrochloride*, $C_{14}H_{10}O_2NCl,HCl$, which forms pale yellow leaflets melting at 196°.

In the preparation of both pyrophthalones by condensation in a sealed tube, a small quantity of an aldol-like bye-product is obtained containing 1 mol. of water more than pyrophthalone, and melting at 180° after crystallisation from alcohol.

*iso*Pyrophthalone is reduced by zinc and acetic acid, yielding a yellow oil having the constitution of a primary alcohol. The *platinichloride* forms brown needles melting at 188°, the *aurichloride*, golden leaflets melting at 140°, the *mercurichloride*, long, white needles melting at 167°, the *picrate*, yellow leaflets melting at 134°.

*Bromo*iso*pyrophthalone* crystallises from alcohol-chloroform in large, bright yellow leaflets which melt at 153°; its *dibromide* melts at 285°. *Nitro*iso*pyrophthalone*, prepared by nitration with nitrogen oxides in acetic acid solution, crystallises in white needles melting at 199°.

Pyrophthalone does not react with hydroxylamine or phenylhydrazine, but with aniline forms phthalanil. On the other hand, *iso*pyrophthalone reacts readily. Its *oxime*, $C_{14}H_{10}O_2N_2$, forms yellow leaflets melting at 240°, the *phenylhydrazone*, $C_{20}H_{15}ON_3,2H_2O$, forms brown leaflets which sinter at 123° and melt at 127°. iso*Pyrophthalanil*, $C_{20}H_{14}ON_2$, crystallises from alcohol in garnet-red needles melting at 185°.

On heating *iso*pyrophthalone with a saturated alcoholic solution of ammonia at 200° in a sealed tube, it is converted into *α-pyrophthaline*, $NH{:}C{<}^{C_6H_4}_{O}{>}C{:}CH{\cdot}C_5NH_4$, which crystallises from alcohol in red needles melting at 185° and is readily converted into *iso*pyrophthalone by boiling with dilute acids. The *hydrochloride* forms slender, orange needles melting at about 261°, the *platinichloride*, reddish-yellow needles melting and decomposing at 222°, the *thallichloride*, red needles melting at 180°, the *aurichloride*, yellow needles sintering at 190° and melting at 195°, the *mercurichloride*, red needles melting and decomposing at 250°, the *picrate*, brown needles melting at 226°.

β-Pyrophthaline, $CO{<}^{C_6H_4}_{NH}{>}C{:}CH{\cdot}C_5NH_4$, prepared by heating together α-picoline and phthalimide in presence of zinc chloride, crystallises from alcohol in yellow leaflets which melt at 255° and are only converted into *iso*pyrophthalone by long boiling with strong hydrochloric acid. The *hydrochloride* forms yellow leaflets which melt at 208°, the *platinichloride*, yellow needles melting at 210°, the *thallichloride*, *aurichloride*, and *mercurichloride*, yellow needles melting at 203°, 212°, and 220° respectively, and the *sulphate*, yellow needles melting at 182—183°.

Attempts to condense α-picoline with succinic anhydride and succinimide were unsuccessful. C. H. D.

Condensation of Quinaldine and Lepidine with Aldehydes. Karl Loew (*Ber.*, 1903, 36, 1666—1671).—o-*Nitrobenzylidenequinaldine* [2-o-*nitrostyrylquinoline*], $C_9NH_6{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, prepared by heating together 2-methylquinoline and *o*-nitrobenzaldehyde in a

sealed tube at 130—140°, separates from alcohol in large, yellow crystals which melt at 103°. The *hydrochloride* forms felted, yellow needles melting at 253°, the *nitrate*, yellow needles melting at 178°, the *sulphate* melts at 238°. The *platinichloride* forms brown, microscopic crystals melting at 223°; the *mercurichloride*, long, yellowish-green crystals melting at 235°, the *aurichloride*, yellow, felted needles melting at 241°, and the *thallichloride*, iridescent leaflets melting at 228°. The *picrate* forms yellow, felted needles. The base reacts with bromine in carbon disulphide solution to form a *bromo*-derivative, which crystallises from methyl alcohol in yellow needles melting at 274°.

2-o-*Nitro-α-hydroxydihydrostyrylquinoline*,

$$C_9NH_6{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NO_2,$$

prepared by heating quinaldine with *o*-nitrobenzaldehyde and water in a sealed tube at 85—90°, crystallises from alcohol in silvery leaflets which melt at 168°. The *hydrochloride* forms white needles melting at 249°; the *mercurichloride*, orange-red leaflets melting at 185°, the *platinichloride*, reddish-brown crystals melting at 180°, and the *aurichloride*, yellow, felted needles melting at 132°.

o-*Nitrobenzylidenelepidine* [4-o-*nitrostyrylquinoline*], prepared by heating 4-methylquinoline with *o*-nitrobenzaldehyde at 130—140°, crystallises from alcohol in yellow, iridescent leaflets which melt at 162°. The *hydrochloride* forms bright yellow leaflets melting at 257—258°, the *nitrate*, yellow needles melting at 178°, the *mercurichloride*, yellow, hair-like needles melting at 244°, the *platinichloride*, small, yellow crystals melting at 262°, and the *aurichloride*, yellow leaflets melting at 235°. The *methiodide* separates from alcohol in red crystals which melt at 237°. With bromine in carbon disulphide it yields a *bromo*-derivative which separates from alcohol in thick, yellow needles melting at 243°. 4-p-*Nitrostyrylquinoline*, prepared from *p*-nitrobenzaldehyde in a similar manner to the *o*-compound, crystallises from alcohol in small, yellow needles which melt at 221°. The *hydrochloride* and *hydrobromide* form yellow needles and melt at 272° and 297° respectively. The *mercurichloride* forms microscopic, yellow crystals melting at 240—241° and sintering at 235°; the *platinichloride* forms small, yellow-brown crystals darkening at 270° without melting; and the *picrate*, felted, yellow needles melting at 287°.

The product of condensation of 4-methylquinoline with cuminaldehyde is uncrystallisable; its *hydrochloride*, $C_{20}H_{19}N{\cdot}HCl,H_2O$, forms bright yellow needles, sinters at 140°, and melts at 217°. The *platinichloride* forms yellow crystals melting at 242°, and the *aurichloride* brownish-red crystals melting at 178°. C. H. D.

Action of *m*-Xylylene Bromide on Primary, Secondary, and Tertiary Amines, and on Potassium Cyanate and Thiocyanate.

GUSTAV HALFPAAP (*Ber.*, 1903, 36, 1672—1682).—*m*-Xylylene bromide combines readily with amines, forming *m*-xylylenediamine derivatives, no case of ring-formation being observed. m-*Xylylenedianthranilic acid*, $C_6H_4(CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H)_2$, is obtained by combination in alcoholic solution as a bright yellow, microcrystalline precipitate melting and decomposing at 247°. On dissolving in potassium

carbonate solution and crystallising the product from alcohol, the *potassium* salt is obtained in large, white, star-shaped crystals melting at 123°. The *calcium* and *ferric* salts are described. m-*Xylylenediïsobutylamine*, $C_6H_4[CH_2{\cdot}N(C_4H_9)_2]_2$, is a yellow oil, the hydrochloride and sulphate of which are also oily. The *mercurichloride* forms white prisms melting at 207°; the *platinichloride*, orange, globular masses melting at 209°, and the *picrate*, dark yellow, quadratic plates melting at 134°. m-*Xylylenedidiamylamine*, $C_6H_4[CH_2{\cdot}N(C_5H_{11})_2]_2$, is a viscid, red oil; the *platinichloride* forms orange needles melting at 149° and the *picrate* bright yellow needles melting at 173°.

m-*Xylylenedidiphenylamine*, $C_6H_4(CH_2{\cdot}NPh_2)_2$, forms bright green needles which become darker in the air, dissolve readily in chloroform, ether, or benzene, and melt at 116°. It has no basic properties and does not form salts.

m-*Xylylenedipiperidine*, $C_6H_4[CH_2{\cdot}C_5NH_{10}]_2$, is a viscid, brown oil; its *hydrochloride* forms white leaflets melting at 156°, the *platinichloride* reddish-yellow prisms melting at 223°, and the *picrate* needles grouped in stellate forms melting at 201°.

m-*Xylyleneditripropylammonium bromide*, $C_6H_4(CH_2{\cdot}NPr^{\alpha}{}_3Br)_2$, crystallises in white prisms which melt at 226° and dissolve readily in water, alcohol, and chloroform. Bromine water added to the alcoholic solution precipitates the *perbromide*, $C_{26}H_{50}N_2Br_6$, which crystallises from hot alcohol in long, orange needles and melts at 160°. The bromide is converted into the *chloride* by shaking with moist silver chloride, and this yields a *platinichloride* forming small, red prisms melting and decomposing at 217°. The *picrate* separates from acetone in short, yellow crystals and melts at 160°.

m-*Xylyleneditriamylammonium bromide*, $C_6H_4[CH_2{\cdot}N(C_5H_{11})_3Br]_2$, is highly deliquescent; it forms a *perbromide* melting at about 95—96°. The *picrate* of the base is yellow and melts at 146°. m-*Xylylenedipyridinium bromide*, $C_6H_4(CH_2{\cdot}C_5NH_5Br)_2$, forms small, white needles melting at 264°; the *perbromide* forms yellow needles and melts at 156°; the *platinichloride* is amorphous and melts at 255°, and the *picrate* forms yellow needles melting at 214°. m-*Xylylenediquinolinium bromide*, $C_6H_4(CH_2{\cdot}C_9NH_7Br)_2$, forms microscopic, pale yellow needles which melt and blacken at 276°. The *perbromide* forms small, red leaflets melting at 128°; the *platinichloride* is amorphous and melts at 230°; the *picrate* crystallises in felted, yellow needles and melts at 205°.

m-*Xylylenedistrychninium bromide*,

$$C_6H_4(CH_2{\cdot}C_{21}H_{22}O_2N_2Br)_2,6MeOH,$$

separates from methyl alcohol in white crystals which char at 250° without fusion. The *picrate* forms small needles and melts at 210°.

m-*Xylylene dithiocyanate*, $C_6H_4(CH_2{\cdot}SCN)_2$, prepared from *m*-xylylene bromide and potassium thiocyanate, crystallises from alcohol in very large prisms melting at 62°, dissolving in alcohol, ether, and chloroform, but not in water, and giving no coloration with ferric chloride. Nitric acid oxidises it to terephthalic acid.

m-*Xylylenediurethane*, $C_6H_4(CH_2{\cdot}NH{\cdot}CO_2Et)_2$, from *m*-xylylene bromide and potassium cyanate in alcoholic solution, is precipitated by water as a flocculent, white mass melting at 160°. C. H. D.

[Derivatives of Diaminodiphenylmethane.] WILHELM EPSTEIN (D.R.-P. 139989).—When 4 : 4′-diaminodiphenylmethane or its alkyl derivatives are nitrated in sulphuric acid solution, the product is generally a 2 : 2′-dinitro-derivative. In order to obtain a mono-nitrated product, an excess of base must be employed, the base and nitro-compound being then separated by fractional precipitation.

2-*Nitro*-4 : 4′-*diaminodiphenylmethane* crystallises from alcohol in sulphur-yellow needles with a satin lustre; it melts at 100—101°. 2-*Nitro*-4 : 4′-*tetramethyldiaminodiphenylmethane* separates from alcohol in groups of red pyramids which melt at 96—96·5°. The corresponding *dinitro*-compounds are orange-coloured, 2 : 2′-*dinitro*-4 : 4′-*tetraethyldiaminodiphenylmethane* separates from alcohol in red leaflets melting at 121—121·5° and showing microscopic laminations. All these compounds yield brown or black dyes when fused with sulphur and sodium sulphide. C. H. D.

Molecular Rearrangement of Thiocyanoacetanilides into Labile ψ-Thiohydantoins: and the Molecular Rearrangement of the Latter into Stable Isomerides. II. TREAT B. JOHNSON [and, in part, with W. K. WALBRIDGE, D. F. MCFARLAND, and W. B. CRAMER] (*J. Amer. Chem. Soc.*, 1903, **25**, 483—491).—Wheeler and Johnson (Abstr., 1902, i, 758) have studied the transformation of thiocyanoacetanilides into labile ψ-thiohydantoins and the subsequent formation of stable isomerides from the latter. The structure of the intermediate products has not yet been settled.

Chloroacetyl-β-naphthalide, $CH_2Cl\cdot CO\cdot NH\cdot C_{10}H_7$, obtained by the action of chloroacetyl chloride on β-naphthylamine, separates from dilute alcohol in rosettes or fine needles melting at 117—118°. It interacts with potassium thiocyanate to form the *labile β-naphthyl-ψ-thiohydantoin*; this crystallises in small prisms, which melt at 147° and reacts with thioacetic acid in benzene solution to give the *acetyl* derivative (4-*keto*-2-*acetylimino*-3-β-*naphthyltetrahydrothiazole*),

$$CO<\begin{matrix}CH_2\text{——}S\\ N(C_{10}H_7)\cdot C{:}NAc\end{matrix},$$

which forms needles melting at 139—140°; as a bye-product, β-naphthylacetothiohydantoic acid is obtained; this melts with intumescence at temperatures varying from 167° to 173°. When the labile β-naphthyl-ψ-thiohydantoin is boiled with dilute alcohol, it undergoes rearrangement into the stable isomeride melting and decomposing at 213—214°.

When ammonium chloroacetate is boiled with β-naphthylthiocarbamide in alcoholic solution, *β-naphthyl-ψ-thiohydantoic acid* is formed, melting at temperatures varying from 195° to 230°. Warming with glacial acetic acid converts this into the *stable β-naphthyl-ψ-thiohydantoin*, $CO<\begin{matrix}CH_2\cdot S\\ NH\cdot C{:}N\cdot C_{10}H_7\end{matrix}$, the *acetyl* derivative of which crystallises from benzene in fine needles melting at 142—143°. Stable β-naphthyl-ψ-thiohydantoin condenses with benzaldehyde to form 4-*keto*-5-*benzylidene*-2-β-*naphthyliminotetrahydrothiazole*, which separates from alcohol in pale yellow plates melting at 272°.

Chloroacetyl-m-*xylidide*, obtained by the action of chloroacetyl chlor-

ide on *m*-xylidine, separates from alcohol in needles which melt at 151—152°. Whilst chloroacetyl-β-naphthalide interacts with potassium thiocyanate to form the labile hydantoin initially, no thiocyanate being formed, with chloroacetyl-*m*-xylidide no labile hydantoin was formed, but the products were the thiocyanate and the stable hydantoin.

Thiocyanoacetyl-m-*xylidide* separates from water in brilliant prisms melting at 98°. When heated at 100°, it undergoes rearrangement into the stable *m*-xylyl-ψ-thiohydantoin.

m-*Xylylthiohydantoic acid* melts with intumescence at about 179—180° and is converted by glacial acetic acid into the *stable* m-*xylyl-ψ-thiohydantoin*, which crystallises from alcohol in needles melting at 157°. Its *acetyl* derivative melts at 165—166° with slight decomposition.

Chloroacetyl-m-*nitroanilide* crystallises from alcohol in plates melting at 101—102°. With potassium thiocyanate, it forms the *labile* m-*nitrophenyl-ψ-thiohydantoin*, which separates from alcohol in plates melting at 183—184°. A. McK.

Acetylenic Ketones. New Method of Synthesis of Pyrazoles. CHARLES MOUREU and M. BRACHIN (*Compt. rend.*, 1903, **136**, 1262—1265).—By the action of hydrazine (hydrazine sulphate and sodium acetate) on benzoylamylacetylene ($C_5H_{11}\cdot C\vdots C\cdot COPh$) in aqueous alcoholic solution, 3-*phenyl*-5-*amylpyrazole*, $NH<\begin{matrix}N=CPh\\C(C_5H_{11})\end{matrix}>CH$, is formed. It crystallises in small, white prisms, melts at 76°, and is sparingly soluble in the common organic solvents.

In the same way, from acetylphenylacetylene, 5-*phenyl*-3-*methylpyrazole*, $NH<\begin{matrix}N=CMe\\CPh\vdots CH\end{matrix}$, is obtained. It forms long, white needles, is easily soluble in hot water, and melts at 127—127·5°; in acetic acid solution, it absorbs 1 mol. of bromine, and with acetic anhydride gives a derivative melting at 41°. It has been identified with the compound obtained by Sjollema (Abstr., 1894, i, 546) from benzoylacetone and hydrazine.

3 : 5-*Diphenylpyrazole*, $NH<\begin{matrix}N=CPh\\CPh\vdots CH\end{matrix}$, formed from benzoylphenylacetylene and hydrazine, separates from benzene in white needles which melt at 199—200° and sublime at 202°.

Phenylanisylacetylene, $CPh\vdots C\cdot CO\cdot C_6H_4\cdot OMe$, was obtained from anisole and phenylpropiolyl chloride in presence of aluminium chloride. With hydrazine, it gives 3-*phenyl*-5-*methoxyphenylpyrazole*,

$$\begin{matrix}CPh\cdot CH\\N\text{---}NH\end{matrix}>C\cdot C_6H_4\cdot OMe,$$

which crystallises from methyl alcohol in slender, white needles and melts at 163° when quickly heated, but at 170° when warmed slowly.

1 : 3 : 5-Triphenylpyrazole, $NPh<\begin{matrix}N=CPh\\CPh\vdots CH\end{matrix}$, is formed from benzoylphenylacetylene and phenylhydrazine.

The formation of these pyrazoles takes place in two phases: (1)

$CPh:C\cdot CO\cdot Me + NH_2\cdot NH_2 = H_2O + CPh:C\cdot CMe:N\cdot NH_2$, and (2) the acetylenic hydrazone changes into the isomeric form, $NH<\begin{matrix}N\text{——}CMe\\ CPh:CH\end{matrix}$.

J. McC.

Indanthrene. II. Felix Kaufler (*Ber.*, 1903, 36, 1721—1722. Compare this vol., i, 446, and Bohn, *ibid.*, 530).—*Anthracenazine*, $C_{28}H_{16}N_2$, is produced on heating bromoindanthrene, indanthrene, and its first reduction-products with hydriodic acid at 310—350°; it forms long, orange-yellow needles, is fairly soluble in nitrobenzene or anisole, but only sparingly so in chloroform or carbon tetrachloride, begins to sublime at 240°, and melts with blackening and sublimation at about 400°. T. M. L.

Action of Sodium on Nitriles. Reinhold von Walther (*J. pr. Chem.*, 1903, [ii], 67, 445—472. Compare Abstr., 1894, i, 503; Lottermoser, Abstr., 1897, i, 38; and Engelhardt, Abstr., 1897, i, 126).—The action of sodium on benzonitrile in benzene solution in presence of dimethylaniline leads to the formation of tetraphenyldihydrotriazine and cyaphenine; in presence of pyridine or quinoline to the formation of cyaphenine only. The dihydrotriazine is formed in presence of phenol, but cyaphenine in presence of phenol alkyl ethers. The action of sodium on benzonitrile in presence of benzaldehyde leads to the formation of an insoluble *substance* which melts at 180—183° and is hydrolysed to benzoic acid and ammonia by boiling dilute hydrochloric acid.

When treated with aniline and sodium, benzyl cyanide yields phenylphenylethenylamidine, and in presence of dimethylaniline the base cyanbenzyline, $CPh<\begin{matrix}C(CH_2Ph)\cdot N\\ C(NH_2)=N\end{matrix}>C\cdot CH_2Ph$, which crystallises in white needles and melts at 106°.

p-*Chlorophenylbenzenylamidine*, $NH:CPh\cdot NH\cdot C_6H_4Cl$, is obtained by the action of sodium on benzonitrile and *p*-chloroaniline in benzene solution, along with benzo-*p*-chloroanilide by boiling benzonitrile with *p*-chloroaniline hydrochloride, or by the action of phosphorus oxychloride and ammonia on benzo-*p*-chloroanilide. The amidine crystallises from alcohol in white prisms or from light petroleum in glistening, white leaflets, melts at 115—116°, is easily soluble in cold ether or benzene, and is slowly hydrolysed by boiling hydrochloric acid, but easily when the hydrochloride is heated with water at 150°, with formation of benzo-*p*-chloroanilide, which is also formed by the action of benzoic chloride on *p*-chloroaniline in presence of pyridine, crystallises in prisms, and melts at 192—193°. The melting point has been given by previous authors as 183—184°.

p-Chlorophenylbenzenylamidine forms a *hydrochloride* which crystallises in colourless prisms and melts and decomposes at 103—108°, a *sulphanilate* which crystallises in long, broad prisms, and a *nitrite* which crystallises from water, melts and decomposes at 90—111°, gives the nitrite reaction with diphenylamine and sulphuric acid, and yields the amidine on treatment with ammonia. The *acetate* crystal-

lises in colourless prisms; the *picrate* crystallises in brownish-yellow prisms and melts at 183°; the *aurichloride* forms yellow needles and melts at 179—180°; the *platinichloride* melts and decomposes at 212°.

The action of benzoyl chloride on the amidine in presence of pyridine leads to the formation of a *dibenzoyl* derivative,

$$NBz\colon CPh\cdot NBz\cdot C_6H_4Cl,$$

which crystallises in colourless prisms and melts at 169°. The *diacetyl* derivative, formed by the action of acetic anhydride on the amidine, crystallises in feathery aggregates of prisms and melts at 170°.

2-Phenyl-4-ketodihydroquinazoline (Körner, Abstr., 1887, 1044) is formed by the action of isatoic acid or of anthranilic acid on *p*-chlorophenylbenzenylamidine or of anthranilic acid on thiobenzamide. The dihydroquinazoline is easily soluble in aqueous sodium hydroxide, and on addition of mineral acids to the alkaline solution separates as a precipitate, which is easily soluble in excess of the acid. In the crystalline state, the dihydroquinazoline is almost insoluble in acids (compare Körner, *loc. cit.*).

The action of phenylcarbimide on *p*-chlorophenylbenzenylamidine leads to the formation of the *phenylcarbamide* derivative,

$$C_6H_4Cl\cdot NH\cdot CPh\colon N\cdot CO\cdot NHPh,$$

which crystallises in white, glistening needles, melts at 201°, and when heated with dilute sulphuric acid (1 mol.) at 120—130° yields carbon dioxide, ammonia, aniline sulphate, and benzo-*p*-chloroanilide. The *phenylthiocarbamide* derivative crystallises in white prisms and melts at 148—151°. The o-*tolylthiocarbamide* derivative crystallises in needles and melts at 143°. The *allylthiocarbamide* derivative forms silvery needles and melts at 169—171°.

The action of carbon disulphide on *p*-chlorophenylbenzenylamidine leads to the formation of the *thiocyanate* of the amidine and *thiobenzo*-p-*chloroanilide*, which crystallises in small, yellow needles and melts at 146—147°.

Cyanic acid, ethyl carbonate, carbonyl chloride, ethoxymethyleneaniline, diphenyldicarbodi-imide, and cyanamide do not react with the amidine. With picryl chloride, the amidine forms p-*chlorophenyltrinitrophenylbenzenylamidine*, $NH\colon CPh\cdot N(C_6H_4Cl)\cdot C_6H_2(NO_2)_3$, which crystallises in short, yellow, glistening prisms, melts and evolves ammonia at 171°, and is hydrolysed with evolution of ammonia by boiling dilute sodium hydroxide. p-*Chlorophenyltrinitrophenylamine*, which is formed by the action of picryl chloride on chloroaniline, crystallises in scarlet prisms and melts at 170°; it could not be obtained by hydrolysis of the amidine.

The action of hydroxylamine hydrochloride on *p*-chlorophenylbenzenylamidine in boiling aqueous solution leads to the formation of the *amidoxime*, which crystallises from alcohol in transparent crystals containing C_2H_6O, melts at 173—174°, loses the alcohol on exposure to air, or more rapidly at 100°, and then melts at 183—184°. The *sulphate* and *hydrochloride* are soluble in hot water and crystallise in prisms. The *picrate* crystallises in brown, triclinic prisms.

When heated in aqueous solution, aniline hydrochloride and the amidine form aniline and the amidine hydrochloride. At higher

temperatures, ammonium chloride and benzochloroanilide are formed. When heated at 160° in alcoholic solution, aniline hydrochloride and the amidine yield ammonium chloride, ethyl benzoate, aniline, chloroaniline, benzochloroanilide, and benzanilide. The formation of benzanilide is probably due to the action of ethyl benzoate on aniline.

G. Y.

Preparation of a Yellow Acridine Dye. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 141297).—When *2-benzyl*-m-*tolylenediamine* (2 mols.), prepared by the reduction of 4-nitro-2-benzyltoluidine and melting at 80°, is condensed with formaldehyde (1 mol.) in sulphuric acid solution, the product is s-*dibenzyltetra-aminoditolylmethane*, crystallising from alcohol in colourless leaflets which melt at 157°. When heated with sulphuric acid under pressure, this condenses to form 2 : 8-*dibenzylamino*-3 : 7-*dimethylacridine*, together with the corresponding leuco-base. The mixture is converted by fuming sulphuric acid into the *disulphonic acid*, a red powder, dyeing leather yellow. Or the dibenzyltetra-aminoditolylmethane may be first sulphonated and then converted into the dye by heating with dilute sulphuric acid under pressure.

C. H. D.

4 : 4′-Diaminodiphenylcarbamidedisulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 140613).—4 : 4′-*Diaminodiphenylcarbamidedisulphonic acid*,

$$CO[NH{\cdot}C_6H_3(NH_2)(SO_3H)]_2 \; [(NH_2):(SO_3H) = 4:3],$$

prepared either by treating *p*-nitroaniline-3-sulphonic acid with phosgene and reducing the product, or by the action of phosgene on *p*-phenylenediaminesulphonic acid, crystallises in colourless needles which dissolve sparingly in water; when suspended in dilute acids and treated with sodium nitrite, it forms a yellow, insoluble tetrazonium compound, which combines readily with naphthol derivatives, &c.

C. H. D.

Electrochemical Reduction of Stilbene Derivatives. KARL ELBS and R. KREMANN (*Zeit. Elektrochem.*, 1903, 9, 416—419).—"Sun yellow" reduced at a nickel cathode in alkaline solution yields 4 : 4′-azostilbene-2 : 2′-disulphonic acid. The same substance is obtained by the reduction of 4 : 4′-di-nitrostilbene-2 : 2′-disulphonic acid. Further reduction of "sun yellow" yields a colourless solution of a hydrazo-compound, which is oxidised by atmospheric oxygen to *p*-azotoluenedisulphonic acid. Further reduction of this substance in acid solution containing tin chloride leads to the formation of *p*-toluidine-*o*-sulphonic acid. These reactions are in agreement with the view that "sun yellow" is 4 : 4′-azoxystilbene-2 : 2′-disulphonic acid.

Dinitrodibenzyldisulphonic acid is reduced in alkaline solution to 4 : 4′-azodibenzyl-2 : 2′-disulphonic acid.

4 : 4′-Azotoluene-2 : 2′-disulphonic acid is reduced in alkaline solution mainly to the corresponding hydrazo-compound, very little *p*-toluidine-*o*-sulphonic acid being formed; 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid is unchanged in the same circumstances.

4 : 4′-Dinitrostilbene is reduced in alkaline solution to 4 : 4′-azoxy stilbene, which, being almost insoluble, is not further reduced.

When "sun yellow" is submitted to electrolytic reduction in a solution containing hydrochloric acid and tin chloride, it is reduced to 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid; more energetic reduction leads to the formation of *p*-toluidine-*o*-sulphonic acid.

When reduced in the same way, 4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid yields *p*-diaminostilbenedisulphonic acid, whilst 4 : 4′-dinitrodibenzyl-2 : 2′-disulphonic acid and 4 : 4′-dinitrostilbene yield the corresponding diamino-compounds. T. E.

Benzene-*o*-azobenzyl Alcohol and its Transformations into Phenylindazole and Azodiphenylmethane. PAUL FREUNDLER (*Compt. rend.*, 1903, **136**, 1136—1138).—*Benzene-o-azobenzyl alcohol*, $PhN:N \cdot C_6H_4 \cdot CH_2 \cdot OH$, prepared by condensing nitrosobenzene with *o*-aminobenzyl alcohol dissolved in acetic acid, crystallises in silky, orange needles, melts at 77—78°, and is soluble in all the usual solvents except petroleum. A small yield of the alcohol is obtained by reducing a mixture of nitrobenzene and *o*-nitrobenzyl alcohol with zinc dust and sodium hydroxide (compare this vol., i, 371).

When benzene-*o*-azobenzyl alcohol is heated alone at 130° or with sulphuric acid at 80°, it is converted into phenylindazole,

$$C_6H_4<\begin{matrix}N\text{--}\\ | \\ CH\end{matrix}>N \cdot Ph;$$

in the former case, there is also produced a small quantity of *azodiphenylmethane*, $C_6H_4<\begin{matrix}N:N\\ CH_2\end{matrix}>C_6H_4$, the latter condensation being provisionally regarded as occurring in the *o*-position; this crystallises in yellow prisms, melts at 76°, has a pleasant odour, is soluble in ether and light petroleum, and is oxidised by chromic acid to a neutral substance, crystallising in red tablets, which is probably *azobenzophenone*. T. A. H.

Nitrogen in Proteids. THOMAS B. OSBORNE and ISAAC F. HARRIS (*J. Amer. Chem. Soc.*, 1903, **25**, 323—353).—Estimations by Hausmann's method (*Zeit. physiol. Chem.*, 1899, **27**, 92) were made as follows: the proteid (about 1 gram) was boiled with 20 per cent. hydrogen chloride for 6—7 hours, the solution evaporated to 2—3 c.c., diluted with about 350 c.c. of water, and distilled with a slight excess of magnesia. After estimating the ammonia, the residue in the flask was filtered and the nitrogen in the filter estimated. The filtrate was evaporated to 100 c.c., cooled to 20°, and treated with sulphuric acid (5 grams), and then with 30 c.c. of a solution containing phosphotungstic acid (20 grams) and sulphuric acid (5 grams per 100 c.c.). After 24 hours, the solution was filtered, washed with a solution containing 2·5 grams of phosphotungstic acid and 5 grams of sulphuric acid per 100 c.c. The washing was done by rinsing the precipitate into a beaker and returning to the filter three successive times. The filtrates amounted to about 200 c.c. The nitrogen was estimated by digesting the precipitate in a 600 c.c. Jena flask with 35 c.c. of

sulphuric acid for 7—8 hours, crystals of potassium permanganate being added from time to time. The remaining nitrogen, chiefly as monoamino-acids, was calculated by subtracting the nitrogen estimated in the above processes from the total nitrogen of the proteid.

The results of estimations with a large number of substances are given. Whilst the maximum and minimum of the total nitrogen differ by 3·49, or 18·3 per cent. of the maximum, the difference between the maximum and minimum basic nitrogen is 6·34, or 92·7 per cent. of the maximum. The amounts of ammonia also differ greatly, whilst the non-basic nitrogen is even more regular than the total nitrogen. N. H. J. M.

The Carbohydrate Group in the Proteid Molecule. Thomas B. Osborne and Isaac F. Harris (*J. Amer. Chem. Soc.*, 1903, **25**, 474—478).—Molisch's furfuraldehyde reaction was applied to various animal and vegetable proteids. A positive reaction was given by globulin, glutenin, hordein, ovalbumin, gliadin, vignin, nucleovitellin, leucosin, and phaseolin, the names being placed in the order of increasing intensity of reaction. The other proteids tested gave either no reaction or one so slight as to be probably due to impurity only. An attempt was also made to estimate quantitatively the amount of furfuraldehyde formed by boiling the proteids with hydrochloric acid, and by adding phloroglucinol to the distillate; ovalbumin was the only proteid which gave a positive result. The evidence for a carbohydrate group in the proteid molecule based on the Molisch reaction cannot be accepted as conclusive. A. McK.

Chemical Relations between Proteids and Aniline Dyes. Martin Heidenhain (*Pflüger's Archiv*, 1903, **96**, 440—472).—After prolonged dialysis of commercial serum-albumin, a certain amount of proteid is precipitated. The proteid which remains in solution has increased acidity. Addition of basic dyes to this causes precipitation. The dialysing tubes are chemically active. The alkali salts of many alizarins do not diffuse, or only slightly. Many of them give specific colours with salt-free proteids, forming chemical combinations; in some circumstances, they precipitate proteids; they split off basic groups from the proteid. The proteid precipitable by dialysis dissolves in acid and basic dyes. The aminoazo-dyes (Congo, &c.) do not diffuse; the chromotropes and typical acid dyes (such as palatine red, &c.) diffuse with difficulty. The chromotropes without acidification act on proteids like the alizarins; so also do acid dyes. W. D. H.

Hydrolysis of Albumin. Max Siegfried (*Chem. Centr.*, 1903, i, 1144—1146; from *Ber. math.-phys. Kl. kön. sächs. Ges. Wiss.*, 1903, 63—87. Compare Abstr., 1902, i, 654).—Glue peptone has $[\alpha]_D$ −101° at 20°, but the hydrochloric acid solution of the product obtained by the action of dilute hydrochloric acid on this peptone is dextrorotatory. On boiling the peptone with a 12·5 per cent. solution of hydrochloric acid, the change takes place in 15 hours, but when a 12·5 per cent. solution of hydrochloric acid containing 20 per cent.

of stannous chloride is used, the lævorotatory power never entirely disappears, but only gradually decreases until it attains a constant value after about 118 hours. The decomposition by hydrochloric acid, therefore, reaches a limit after a certain time, intermediate products being formed which resist the further action of the acid. One of these intermediate products, *glutokyrine*, $C_{21}H_{39}O_8N_9$, has been isolated. It is best prepared in large quantities by the action of acid on gelatin. It is a strong base, has an alkaline reaction, absorbs carbon dioxide from the air, and gives the biuret reaction. The *sulphate*, $(C_{21}H_{39}O_8N_9)_2,5H_2SO_4$, prepared by dissolving the base in very dilute sulphuric acid and precipitating with alcohol, is very readily soluble in water, forming an acid solution to which Congo-red is also sensitive. The *hydrochloride* is readily soluble in water or alcohol. The *platinichloride* is readily soluble in water, but is precipitated from its aqueous solution on the addition of alcohol and ether in pale brown flakes; its composition does not appear to be constant. The *phosphotungstate* crystallises from water in very small aggregates of slender needles; it is readily soluble in hot, but only sparingly so in cold, water. The *β-naphthalenesulpho*-derivative of glutokyrine, $C_{21}H_{34}O_8N_9(C_{10}H_7SO_2)_5,H_2O$, prepared by Fischer and Bergell's method (this vol., i, 24), separates in white flakes, melts at 137—138°, and is very sparingly soluble in water, soluble in alcohol, methyl alcohol, or chloroform, but insoluble in benzene, light petroleum, or carbon disulphide. Glutokyrine prepared from glue and that from gelatin yield identical β-naphthalenesulpho-derivatives.

The results of numerous experiments on boiling glutokyrine with mixtures of 1 part by weight of sulphuric acid and 2 of water or with hydrochloric acid for 12—60 hours show that the basic groups or complexes play a more important *rôle* in glutokyrine than in peptones. The product obtained by hydrolysis contains arginine, lysine, glutamic acid, and probably glycollic acid. The presence of histidine could not be detected. Quantitative experiments show that 1 molecule of glutokyrine yields 1 molecule each of arginine, lysine, and glutamic acid, and 2 of glycollic acid. These experiments confirm, to some extent, Kossel's theory of the existence of a basic nucleus in the proteid molecule. In the case of glue, equal molecular proportions of lysine and arginine, together with small quantities of amino-acids, do undoubtedly form a complex which is gradually split off by the moderate action of dilute acids forming substances which resist the further action of the acid. The protamines of fish spermatozoa are possibly formed by the polymerisation or condensation of kyrine or similar decomposition products of the proteids. E. W. W.

Hydrolysis of Crystallised Oxyhæmoglobin from Horses' Blood. Emil Abderhalden (*Zeit. physiol. Chem.*, 1903, 37, 484—494. Compare this vol., i, 136).—In addition to the compounds previously enumerated, the following new products have been detected: tyrosine, cystine, serine (Abstr., 1902, i, 268; this vol., i, 25), lysine, arginine, histidine (Abstr., 1901, i, 107), tryptophan, and hydroxypyrrolidine-2-carboxylic acid (Abstr., 1902, i, 699). The relative amounts of the different products are alanine, 4·02; leucine, 27·82; pyrrolidine-2-carb-

oxylic acid, 2·25; phenylalanine, 4·06; glutamic acid, 1·66; aspartic acid, 4·25; cystine, 0·3; serine, 0·54; hydroxypyrrolidine-2-carboxylic acid, 1·0; tyrosine, 1·28; lysine, 4·1; histidine, 10·5; arginine, 5·2; and leucinimide, 0·92 per cent. of the oxyhæmoglobin used.

The leucinimide is probably a secondary decomposition product obtained from the leucine (compare Salaskin, Abstr., 1901, i, 622).

J. J. S.

Hydrolysis of Crystallised Serum-albumin from Horses' Blood. Emil Abderhalden (*Zeit. physiol. Chem.*, 1903, **37**, 495—498).—The following products have been obtained by hydrolysis with fuming hydrochloric acid of sp. gr. 1·19. Alanine, 2·68; leucine, 20·00; pyrrolidine-2-carboxylic acid, 1·04; phenylalanine, 3·08; glutamic acid, 1·52; aspartic acid, 3·12; cystine, 2·3; serine, 0·6; and tyrosine, 2·1 per cent. Tryptophan is also present. The method of procedure was the same as with oxyhæmoglobin. J. J. S.

Hydrolysis of Edestin. Emil Abderhalden (*Zeit. physiol. Chem.*, 1903, **37**, 499—505).—When hydrolysed with fuming hydrochloric acid and then esterified by Fischer's method, edestin has been found to yield the following products: glycine, 3·8; alanine, 3·6; leucine, 20·9; pyrrolidine-2-carboxylic acid, 1·7; phenylalanine, 2·4; glutamic acid, 6·3; aspartic acid, 4·5; cystine, 0·25; serine, 0·33; hydroxypyrrolidine-2-carboxylic acid, 2·0; tyrosine, 2·13; lysine, 1·0; histidine, 1·1; and arginine, 11·7 per cent.; tryptophan is also present. The products and also the amounts are similar to those obtained from oxyhæmoglobin and serum albumin (compare preceding abstracts). J. J. S.

Formation of Carbamide by the Oxidation of Albumin with Permanganate according to Jolles. Emil Abderhalden (*Zeit. physiol. Chem.*, 1903, **37**, 506—507. Compare Jolles, Abstr., 1901, i, 583; 1902, i, 86, 331; Schulz, 1901, i, 780).—The author cannot confirm Jolles' results, even when following his directions in every detail. J. J. S.

Hydrolysis of Zein by Hydrochloric Acid. Leo Langstein (*Zeit. physiol. Chem.*, 1903, **37**, 508—512. Compare Kossel and Kutscher, *ibid.*, 1900, **31**, 165; Szumowski, Abstr., 1902, ii, 674).—When hydrolysed and esterified by Fischer's method, zein yields alanine, 0·5; leucine, 11·25; pyrrolidine-2-carboxylic acid, 1·49; phenylalanine, 6·96; glutamic acid, 11·78; and aspartic acid, 1·04 per cent. No other proteid yields so large a percentage of phenylalanine. Glycine could not be isolated, but the presence of aminovaleric acid was shown. The presence of arginine, histidine, tyrosine, and a carbohydrate nucleus has also been demonstrated. J. J. S.

Action of Radium Salts on Globulin. W. B. Hardy (*Proc. physiol. Soc.*, 1903, xxix—xxx; *J. Physiol.*, **29**).—If a globulin solution is exposed to the radiations from radium bromide through two sheets of mica, no effect is observed. But if unscreened drops are used, the

opalescence of an electro-positive (acid) solution of globulin diminishes. An electro-negative (alkaline) solution is turned into a jelly, at first transparent and then opaque. This occurs in about three minutes. The emanations from radium are (1) those having the mobility of a heavy gas; (2) positively charged particles of slight penetrative power, and relatively large size; and (3) ultra-material negatively charged particles. A mica plate will screen off (1) and (2), but (3) has no effect on the globulin. Reasons are given for believing that the action observed is certainly due to (2). The physiological influences of radium discharges on the living tissues seem to be limited to a superficial layer a few millimetres deep. W. D. H.

The Pigment of Hair. EDUARD SPIEGLER (*Beitr. chem. Physiol. Path.*, 1903, **4**, 40—58).—Empirical formulæ are given for the pigments obtained from various kinds of hair; for instance, for that from black horsehair, $C_{50}H_{58}O_{12}N_8S$; from black sheep's wool, $C_{48}H_{60}O_{20}N_8S$; from white sheep's wool, $C_{61}H_{98}O_{20}N_{10}S$. The white pigment is believed to be a chromogen of the dark. The theory of the origin of such pigments from hæmoglobin is combated, mainly because hæmopyrrol and hæmatic acid are not obtainable from it. W. D. H.

Presence of Cadaverine in the Products of Hydrolysis of Muscle. ALEXANDRE ÉTARD and A. VILA (*Compt. rend.*, 1903, **136**, 1285—1286).—By the isolation of the benzoyl derivative, it has been proved that cadaverine results from the hydrolytic decomposition of muscle with 15 per cent. sulphuric acid. J. McC.

Chondroitin-sulphuric Acid and the Presence of a Hydroxyamino-acid in Cartilage. I. A. ORGLER and CARL NEUBERG (*Zeit. physiol. Chem.*, 1903, **37**, 407—426. Compare Schmiedeberg, *Arch. Exp. Pathol.*, 1891, **28**, 355).—Molecular weight determinations of chondrosin sulphate by the ebullioscopic and cryoscopic methods give values ranging from 1633—2022, which are much higher than those required for Schmiedeberg's formula. Chondroitin-sulphuric acid and its products of hydrolysis do not give any of the reactions for glycuronic acid. The acid obtained by Schmiedeberg by the hydrolysis of the sulphuric acid with barium hydroxide and described by him as glycuronic acid is a *hydroxyamino-acid* and has been isolated in the form of its *cupric* salt, $[C_6H_6O_2(OH)_4(NH_2)]_2Cu$. It is probably a *tetrahydroxyaminohexoic acid.* The acid itself has not been obtained in a crystalline form. When boiled with barium hydroxide solution, it yields ammonia and also gives the pine-wood test. It does not reduce Fehling's solution and does not give the Molisch test. Oxides of copper and iron dissolve in the acid, and it also yields a crystalline *cadmium* salt. It is precipitated by lead acetate and ammonia and partially by mercuric acetate, barium hydroxide, and silver nitrate. Solutions of the acid are feebly dextrorotatory, and it appears to resemble the acid described by Langstein (Abstr., 1902, i, 331). The carbohydrate with which this acid is condensed in chondrosin is not glucosamine. The barium salt, $(C_4H_7O_5)_2Ba$, obtained by Schmiedeberg and supposed to be formed

from glucosamine is in reality produced from the hydroxyamino-acid and is not identical with the salt, $(C_4H_7O_5)_2Ba,2H_2O$, obtained from glucosamine sulphate, which is now shown to be barium *d*-erythronate.

J. J. S.

Constitution of Tryptophan. F. GOWLAND HOPKINS and SYDNEY W. COLE (*J. Physiol.*, 1903, **29**, 451—466).—Tryptophan is scatoleaminoacetic acid. Under the influence of anaërobic bacteria, it yields scatoleacetic acid, and under that of aërobic growths, scatolecarboxylic acid, scatole, and indole.

W. D. H.

Diastatic Hydrolysis of Salol. EMM. POZZI-ESCOT (*Compt. rend.*, 1903, **136**, 1146—1147).—Salol is hydrolysed by the lipase of castor-oil seeds much more slowly than is ethyl butyrate. This difference is not due to inhibiting action by the salicylic acid formed, since the activity of lipase is not diminished by the presence of phenol.

T. A. H.

Reaction of Oxydases with Hydrogen Peroxide. C. GESSARD (*Compt. rend. Soc. Biol.*, 1903, **55**, 637—639).—Laccase and tyrosinase are characterised by colour reactions, the former by the blue colour it gives with guaiacum, the latter by the red colour becoming black with tyrosine. The addition of hydrogen peroxide prevents or hinders the laccase reaction, although other ferments which render the reagent blue are not affected. Hydrogen peroxide does not influence the test for tyrosinase.

W. D. H.

Hydrolysis of Acid Imides and Amic Acids by Ferments. MAX GONNERMANN (*Pflüger's Archiv*, 1903, **95**, 278—296. Compare Abstr., 1902, i, 512).—Oxamic acid is not hydrolysed by any of the ferments previously mentioned. Succinimide, dibenzamide, and phthalimide are hydrolysed by pepsin; succinimide and phthalimide by trypsin; phthalimide by emulsin; succinimide, succinamic acid, dibenzamide, and phthalimide by finely-divided sheep's liver, and dibenzamide, disalicylamide, and phthalimide by the finely-divided nerves of sheep.

Ptyalin, invertase, and maltase have no action on any of the compounds investigated.

Parabanic acid is readily decomposed, yielding oxalic acid, by the action of aqueous ammonia or sodium carbonate at relatively low temperatures, and also when an aqueous solution is heated at 60°.

J. J. S.

Enzymes of Milk. NEUMANN WENDER (*Chem. Centr.*, 1903, i, 592; from *Oesterr. Chem.-Zeit.*, **6**, 1—3).—A solution of guaiacum resin or a tincture of guaiacum wood only gives a blue coloration with milk after the solution has been exposed for some time to the action of air and light, whereby hydrogen peroxide, or a similar peroxide, is formed. The presence of the peroxide is readily detected by means of tetramethyl-*p*-phenylenediamine hydrochloride and diastase solution.

Galactase, as ordinarily prepared from milk, is not a homogeneous enzyme, but consists of milk-trypsin or galactase, milk-catalase, and

milk-peroxydase. The trypsin has proteolytic properties, dissolves casein, and becomes inactive at 76°. The catalase destroys hydrogen peroxide and loses its activity at 80°. The peroxydase is an anaëroxydase, is capable of removing oxygen from peroxides and transferring it to oxidisable substances, gives a blue coloration with guaiacum tincture and hydrogen peroxide, and becomes inactive at 83°. Utz's method of distinguishing fresh from boiled milk by means of ursol-*D* (this vol., ii, 114) has proved most satisfactory, and depends on the presence of a peroxydase; other materials which contain peroxydase, such as the bast of horse-chestnuts, beetroot, &c., also give this reaction.

E. W. W.

Law of the Action of Trypsin on Gelatin. VICTOR HENRI and LARGUIER DES BANCELS (*Compt. rend.*, 1903, 136, 1088—1090).—When trypsin, in presence of kinase (intestinal extract), is allowed to act on gelatin solutions, the electrical conductivity of the latter increases regularly, and the variation is independent of the concentration of the solution. This affords a trustworthy method of investigating the progress of this reaction, and the observations recorded show that the action of trypsin on gelatin is of the same character as that of enzymes on carbohydrates, proceeding by the formation of intermediate compounds.

T. A. H.

Experiments on Yeast Extract. JAKOB MEISENHEIMER (*Zeit. physiol. Chem.*, 1903, 37, 518—526. Compare Macfadyen, Morris, and Rowland, Abstr., 1901, i, 59; Buchner, Abstr., 1899, ii, 606).—Even when yeast extract is considerably diluted (1 in 25) it still possesses strong fermentative properties. With water alone as the diluent, the activity is largely destroyed, but dilution with 10 per cent. glycerol solution, or even better with 10 per cent. egg-albumin solution, does not destroy the activity.

Impure zymase may be precipitated from yeast extract by the addition of large amounts (10 to 1) of acetone, and the product thus obtained is similar in all respects to that obtained by the use of ether and alcohol. Ahren's method (Abstr., 1900, ii, 610) for the concentration of yeast extracts by freezing is a good practical method. It is not necessary to press out the ice, but merely to thaw the frozen mass very gradually without shaking; the concentrated coloured extract will be found at the bottom of the vessel and pure water at the top. Trommsdorff's statement that the proteids undergo a change during extraction from the yeast is incorrect as the dry residue gives the same reaction with Gram's reagent as the yeast itself, and it is thus probable that the blue coloration is due to an insoluble substance which is not present in the extract.

Small amounts of acetic and lactic acids are formed during the fermentation of sugar solutions with the extract freed from yeast cells.

J. J. S.

Silicon Compounds. II. WALTHER DILTHEY (*Ber.*, 1903, 36, 1595—1600. Compare this vol., i, 405).—Benzoylacetone reacts with an absolute ethereal solution of silicon chloride, and on the addition of

water yields oily drops of a compound which gradually solidifies. This product reacts as though it were tribenzoylacetonylsilicon chloride hydrochloride, X_3SiCl_2H ($X = COPh\cdot CHAc\cdot$).

Its chloroform solution reacts with anhydrous ferric chloride evolving hydrogen chloride and yielding a mixture of two *ferrichlorides* of the formula $X_3SiFeCl_4 = C_{30}H_{27}O_6Cl_4SiFe$. The one crystallises in long needles melting at 173° and the other in compact prisms melting at 188°. Both are insoluble in ether, benzene, or light petroleum, but readily soluble in chloroform. The compounds cannot be transformed into one another.

Two isomeric *aurichlorides*, $X_3SiAuCl_4$, also exist; they may be obtained in a crystalline form by the addition of ether to the chloroform solution, and must be separated mechanically. The large, yellow, compact prisms melt at 185—187° and the small plates at 164°.

Two isomeric double salts may also be obtained with zinc chloride.

Dibenzoylmethane and silicon chloride react yielding the compound X_3SiCl [$X = (COPh)_2CH\cdot$] in the form of small, yellow needles or plates, melting above 300° and readily soluble in glacial acetic acid or chloroform. With ferric chloride, it forms a *double* salt, $X_3Si(FeCl_4)$, which crystallises in yellow needles melting at 252—255°. The *aurichloride*, $X_3SiAuCl_4$, is very stable and crystallises in glistening, golden-yellow, lance-shaped crystals melting at 258—259. J. J. S.

Organic-metallic Derivatives of Nuclear Dihaloid Derivatives of Aromatic Hydrocarbons. F. Bodroux (*Compt. rend.*, 1903, **136**, 1138—1139. Compare this vol., i, 221).—When a solution of *p*-dibromobenzene in boiling ether is treated with bromine in presence of metallic magnesium there is formed p-*bromophenylmagnesium bromide*, $C_6H_4Br\cdot MgBr$; this is decomposed by water with the production of bromobenzene and a small quantity of 4 : 4′-dibromodiphenyl, and by carbon dioxide into *p*-bromobenzoic acid. By a similar reaction, *p*-chlorobromobenzene has been transformed into p-*chlorophenylmagnesium bromide*, and from this chlorobenzene and *p*-chlorobenzoic acid have been obtained. The magnesium derivatives also react with iodine, the magnesium bromide residue being replaced by an atom of iodine; thus, *p*-dibromobenzene has in this way been converted into *p*-bromoiodobenzene. From *p*-dichlorobenzene, no magnesium derivative could be obtained. T. A. H.

Organo-magnesium Compounds. II. Action on Phosgene. Franz Sachs and Hermann Loevy (*Ber.*, 1903, **36**, 1588—1590).—Phosgene reacts with aromatic organo-magnesium compounds in very much the same manner as with the aliphatic compounds (compare Grignard, this vol., i, 455). With an absolute ethereal solution of phenylmagnesium bromide, phosgene yields a crystalline compound which, on treatment with water, is transformed into triphenylcarbinol. The yield is about 50 per cent. Tri-*p*-tolylcarbinol may be obtained in a similar manner. *Tribenzylcarbinol*, obtained from benzylmagnesium bromide and phosgene, distils at 277—278°, melts at 55°, has an odour of orange-blossom, and is readily soluble in most solvents. J. J. S.

Organic Chemistry.

Composition of Roumanian Petroleum. Petrus Poni (*Ann. Sci. Univ. Jassy*, 1903, 2, 65—80).—The presence of methylpropane in petroleum from Colibasi is shown by the fraction boiling between 0° and 10° giving, on bromination, the bromo-derivative, CMe_3Br (m. p. 72°). The fractions boiling between 60° and 100° do not contain secondary hexanes, as on nitration they yield aromatic derivatives only; they therefore differ totally in their nature from similar fractions of Galician petroleum, which contain *iso*hexane and methylpentane (Zaloziecki and Frasch, Abstr., 1902, i, 197); there is, moreover, the difference that the densities of fractions of Roumanian petroleum, taken every 2° between 50° and 70°, diminish to a minimum at 60—62° and then continuously increase, whilst in the case of Galician oil there is a steady increase of density throughout. The Roumanian petroleum resembles in this respect the Russian (Markownikoff, Abstr., 1898, i, 637) and American (Young, Trans., 1898, 73, 909) oils.

Aromatic hydrocarbons were isolated by nitrating the fractions boiling between 64° and 200°. Benzene is present only in small quantities, and is found in the fractions 64—66° and 74—76°; it is carried over completely with the hexanes and methyl*cyclo*pentane, and is not present in the fractions boiling at 76—78° and 88—90°. Toluene is present in small amount in the fractions boiling at 90—100°, and constitutes 22·7 per cent. of the fraction between 100° and 110°. *m*-Xylene is the principal constituent of the liquid boiling between 110° and 144°, and forms 11·2 per cent. of that boiling between 100° and 200°. Mesitylene exists in the fractions between 146° and 158°.

The oil boiling at 160—162° on nitration gave a *trinitro*-derivative, $C_{10}H_{11}(NO_2)_3$, which crystallises from glacial acetic acid, melts at 170—172°, and is not affected by the most energetic oxidising agents. The fractions 170—172° and 176—178° gave, similarly, trinitro-derivatives of the same composition derived from a hydrocarbon, $C_{10}H_{14}$; they melt at 181—182° and 155—157° respectively, the former being less soluble in alcohol than the latter.

A curve is given showing the variation in density of the fractions boiling between 85° and 200°, from which the aromatic compounds have been removed by nitration; there is a maximum at 100—102°, due to methyl*cyclo*hexane, and a minimum at 116—118°, due to some undetermined paraffin. A second maximum at 132—134° corresponds with ethyl*cyclo*hexane, and a second minimum at 140—142° with another paraffin. Finally, there is a third maximum at 158—160°, and between 160° and 172° the curve is almost horizontal, but subsequently it rises continuously and rapidly until the temperature 200° is reached. W. A. D.

Pyrogenetic Contact Reactions of Organic Compounds. IV. A New Method of Preparing Olefines. Wladimir Ipatieff (*Ber.*, 1903, 36, 1990—2003. Compare Abstr., 1902, i, 4, 335).—When alcohol vapour is passed through a glass or copper tube filled

with powdered graphite or silica and heated at 600°, very little decomposition occurs, but alumina acts as a powerful catalyst, and at 350° causes 98 per cent. of the alcohol to be resolved into ethylene and water. The decomposition of alcohol, on being slowly passed through a platinum tube at 610—630°, is of a different character, 23 per cent. of the whole being decomposed, 17 per cent. into aldehyde and hydrogen, and 6 per cent. into ethylene and water; the majority of the aldehyde, however, at this temperature undergoes a further resolution into carbon monoxide and methane. Ordinary metallic copper, when heated, does not cause any change in alcohol, but finely-divided copper, freshly reduced from the oxide by alcohol vapour, gives rise at 620° to 10 per cent. of aldehyde; similar results are obtained with lead and nickel oxides. Metallic zinc commences to decompose alcohol at 520°, and at 540—550° an almost complete conversion into aldehyde and hydrogen is effected, only a very small proportion of ethylene being formed.

Normal propyl alcohol is transformed by alumina at 560° almost quantitatively into propylene and water, and with *iso*propyl alcohol at 360°, 96 per cent. of the product consists of propylene and 4 per cent. of hydrogen. With *iso*butyl alcohol and alumina at 500°, practically pure *iso*butylene is obtained, whilst normal butyl alcohol gives *n*-butylene. Ordinary amyl alcohol at 540° gives 92 per cent. of the theoretical quantity of an amylene consisting of β-methyl-Δ^{α}-butylene, $CMeEt{:}CH_2$, *iso*amylene, and β-methyl-Δ^{β}-butylene; the first two of these products are formed directly from the corresponding alcohols, β-methylbutyl alcohol and *iso*butylcarbinol, whilst the third is due to an isomeric change of the α-*iso*amylene, induced by alumina under the conditions of the experiment (compare following abstract). β-Methyl-Δ^{β}-butylene and β-methyl-Δ^{α}-butylene are produced simultaneously by the pyrogenetic decomposition of dimethylethylcarbinol. W. A. D.

Pyrogenetic Contact-Reactions of Organic Compounds. V. Contact Isomerism. WLADIMIR IPATIEFF (*Ber.*, 1903, 36, 2003—2013).—α-*iso*Amylene, which is not appreciably changed by being passed through a glass tube at 500—550°, is converted, to the extent of about 80 per cent., into β-methyl-Δ^{β}-butylene by passage over aluminium oxide at 525—535°, thus: $CHMe_2 \cdot CH{:}CH_2 \rightarrow CMe_2{:}CHMe$; an attempt to reverse the action by passing β-methyl-Δ^{β}-butylene over alumina at 520—550° gives, not α-*iso*amylene, but, along with unchanged material, about 10 per cent. of a hydrocarbon, insoluble in sulphuric acid, which boils at 28—32°.

*iso*Butylene does not undergo isomeric change under the influence of alumina, but at 550—600° gives rise only to hydrogen, paraffins, and some propylene; fused zinc chloride is also without action on the olefine, and the fact that with this reagent at 540—550°, *iso*butyl alcohol gives considerable quantities of α- and β-butylenes as well as of *iso*butylene, must be attributed to an abnormal elimination of water from the alcohol giving initially some methyltrimethylene, which is subsequently transformed isomerically into the two olefines (compare following abstract).

China clay at 5[illegible] converts ethyl alcohol largely into ethylene, and *iso*butyl alcohol into a mixture consisting of five-sixths of *iso*butylene,

and one-sixth of α- and β-butylene; the difference in behaviour in the latter case from that of alumina, which gives *iso*butylene as the sole product, is very striking. W. A. D.

Pyrogenetic Contact Reactions of Organic Compounds. VI. Contact Isomerism. WLADIMIR IPATIEFF and W. HUHN (*Ber.*, 1903, 36, 2014—2016).—Trimethylene is converted into propylene to the extent of 29 per cent. by being slowly passed over platinum sponge at 315°; at 200°, the conversion is only 5 per cent., and with aluminium oxide at 370—385° it is about 20 per cent. The passage of the same gas through a heated glass tube without a catalyst induces only a very slight change. When 1 : 1-dimethyltrimethylene is passed over aluminium oxide at 340—345°, it is almost completely converted into β-methyl-Δ^{β}-butylene. W. A. D.

Preparation of Carbides and Acetylene Acetylides by the Action of Acetylene on the Alkali and Alkaline-earth Hydrides. HENRI MOISSAN (*Compt. rend.*, 1903, 136, 1522—1525). —When acetylene is passed over potassium hydride at 100°, reaction takes place according to the equation $2C_2H_2 + 2KH = K_2C_2,C_2H_2 + H_2$. The hydride must not be in large crystals, and the gas must be left in contact with the solid for some hours before the reaction is complete. The hydrides of rubidium, cæsium, and calcium are acted on in the same way, the compounds formed being identical with those produced by the action of acetylene on the metal-ammoniums (Abstr., 1899, i, 241; this vol., i, 545). Sodium hydride is not easily acted on, and even after long contact at 100° the sodium acetylide acetylene was mixed with sodium hydride.

Since these compounds decompose in a vacuum at a comparatively low temperature, it is thus easy to prepare the various carbides without the necessity of employing high temperatures.

At 100°, ethylene and methane do not act on these hydrides.

J. McC.

Addition of Halogen Hydrides to Ethylenoid Hydrocarbons in Acetic Acid Solution. WLADIMIR IPATIEFF and OGONOWSKY (*Ber.*, 1903, 36, 1988—1990; *J. Russ. Phys. Chem. Soc.*, 1903, 35, 452—457).—*iso*Butylene, $CMe_2{:}CH_2$, prepared either by heating *iso*butylene iodide with alcoholic potassium hydroxide or by the decomposition of *iso*butyl alcohol by aluminium oxide, when passed into aqueous hydrobromic acid at 0°, gives, as the sole product, *tert.*-butyl bromide; when absorbed, however, by hydrogen bromide dissolved in acetic acid, considerable quantities of primary *iso*butyl bromide, $CHMe_2{\cdot}CH_2Br$ (b. p. 87—95°), are also formed. In acetic acid solution, therefore, Markownikoff's rule is departed from.

W. A. D.

Dibromoacetylene. PAUL LEMOULT (*Compt. rend.*, 1903, 136, 1333—1335).—*Tribromoethylene*, prepared by the addition of sodium ethoxide to tetrabromoethane dissolved in ether, is a colourless oil which can be distilled (*Bull. Soc. chim.*, 1903, iii, 29, 1010). This,

when dissolved in alcohol and treated with a slight excess of potassium hydroxide, is converted into *dibromoacetylene*, C_2Br_2, which can be obtained by distilling in a current of nitrogen and collecting the distillate in water previously freed from oxygen by boiling. It is a colourless, highly unstable liquid which boils at about 80°, has a sp. gr. about 2°, and is soluble in organic liquids. It inflames spontaneously in contact with oxygen, but can be preserved for several weeks under water. Bromine reacts violently with dibromoacetylene, forming tetrabromoethylene; iodine reacts similarly, forming dibromodi-iodoethylene. When oxygen is passed into a solution of dibromoacetylene in ether in presence of water, a violent reaction takes place with the formation of hydrogen bromide and oxalic acid and a bromo-derivative of very irritating odour. T. A. H.

Function of Alcohol in Preserving Chloroform. ADRIAN (*J. Pharm. Chim.*, 1903, [vi], 18, 5—9).—The decomposition of chloroform by light is delayed when ethyl alcohol is present. Chlorinated acetaldehydes are formed instead of the hydrogen chloride and carbonyl chloride produced under ordinary conditions. G. D. L.

Tetranitromethane. AMÉ PICTET and P. GENEQUAND (*Ber.*, 1903, 36, 2225—2227. Compare this vol., i, 395).—Tetranitromethane has a sp. gr. 1·650 at 13°/4° and n_D 1·43985 at 17°. It reacts with alcoholic ammonia, forming the ammonium salt of nitroform, $C(NO_2)_2:NO\cdot ONH_4$, prepared by Hantzsch and Rinckenberger (Abstr., 1899, i, 404) from nitroform and ammonia. C. H. D.

Nitro*iso*butylene. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1903, iii, 29, 517—519. Compare Abstr., 1901, i, 114; 1902, i, 532).—Nitro*iso*butylene, prepared by heating ethyl nitrodimethylacrylate with sodium hydroxide at 50°, is a slightly yellow, mobile liquid of irritating odour; it boils at 80° under 40 mm. pressure and has a sp. gr. 1·052 at 0°/0° (compare Haitinger, Abstr., 1879, 700). T. A. H.

Action of Nitric Acid of Different Concentrations under Pressure on *iso*Pentane. PETRUS PONI and N. COSTACHESCU (*Ann. Sci. Univ. Jassy*, 1903, 2, 119—125. Compare Abstr., 1902, i, 581).—Dilute nitric acid of sp. gr. 1·075—1·14 acts only with difficulty on *iso*pentane at temperatures below 140°, producing β-nitro-β-methylbutane. More concentrated acids (sp. gr. 1·38—1·42) at 60° attack the hydrocarbon more readily, giving nitrated and oxidised products; the best result is obtained with acid of sp. gr. 1·42 in the proportion of 1·5 mols. of acid to 1 mol. of hydrocarbon. The products then are β-nitro-β-methylbutane, which predominates, $\beta\gamma$-dinitro-β-methylbutane, $\beta\gamma\delta$-trinitro-β-methylbutane, α-hydroxy*iso*butyric acid, and oxalic and carbonic acids.

$\beta\gamma$-Dinitro-β-methylbutane, $NO_2\cdot CMe_2\cdot CHMe\cdot NO_2$, boils at 105—110°

under 44 mm. and has a sp. gr. 1·1572 at 0°/0°. *βγδ-Trinitro-β-methylbutane* crystallises from benzene and melts at 179—184°.

W. A. D.

Formula of β-Methyl-Δ^{β}-butylene Nitrosite, Nitrosate, and Nitrosochloride. JULIUS SCHMIDT (*Ber.*, 1903, 36, 1765—1768. Compare Abstr., 1902, i, 581, 582; this vol., i, 2, 3, and Hantzsch, Abstr., 1902, i, 734; this vol., i, 61).—The nitrosites, nitrosates, and nitrosochlorides described by the author behave in exactly the same manner as the undoubted nitroso-compounds described by Bamberger and Seligman, and cannot therefore have the formula suggested by Hantzsch.

T. M. L.

γ-Bromo-β-methyl-Δ^{β}-butylene Nitrosate. JULIUS SCHMIDT and PERCY C. AUSTIN (*Ber.*, 1903, 36, 1768—1774).—*γ-Bromo-β-methyl-Δ^{β}-butylene nitrosate*, $NO_3\cdot CMe_2\cdot CBrMe\cdot NO$, prepared by the action of nitrous fumes on crude γ-bromo-β-methyl-Δ^{β}-butylene, $CMe_2{:}CBrMe$, and purified by fractional crystallisation from light petroleum, crystallises in blue, feathery needles, which are volatile and have a pungent smell, and gives Liebermann's reaction, but does not undergo isomeric change. When heated at 140—150°, or when oxidised with potassium permanganate, it is converted into *bromonitroethyl*iso*propyl nitrate*, $NO_3\cdot CMe_2\cdot CMeBr\cdot NO_2$, which crystallises from alcohol in white prisms and melts at 226° with liberation of nitrous fumes. Concentrated potassium hydroxide at 100° slowly decomposes the nitrosate, but does not bring about isomeric change; the nitrosate does not condense with benzyl cyanide or *m*-nitrobenzyl cyanide.

T. M. L.

Action of Nitrogen Dioxide on Tetramethylethylene [βγ-Dimethyl-Δ^{β}-butylene]. JULIUS SCHMIDT (*Ber.*, 1903, 36, 1775—1777).—βγ-Dimethyl-Δ^{β}-butylene, $CMe_2{:}CMe_2$, does not yield a nitrosite or nitrosate. The principal product of the action of nitrogen dioxide or of nitrous fumes is the *dinitrite*,

$$NO\cdot O\cdot CMe_2\cdot CMe_2\,O\cdot NO,$$

which crystallises from light petroleum in white needles when heated rapidly, melts with liberation of gas at 160°, and gives Liebermann's reaction. The hydrate, $C_6H_{12}N_2O_4,H_2O$, crystallises from dilute alcohol in white needles, sinters below 90°, and melts at 115—116°; potassium hydroxide converts it quantitatively into potassium nitrite and pinacone. A by-product, which is probably the *dinitro*-compound, $NO_2\cdot CMe_2\cdot CMe_2\cdot NO_2$, crystallises from alcohol in pearly flakes and melts with liberation of gas at 213—214°.

T. M. L.

Preparation of Primary Alcohols by means of the Corresponding Acids. LOUIS BOUVEAULT and GUSTAVE BLANC (*Compt. rend.*, 1903, 136, 1676—1678).—The methyl or ethyl esters of the fatty acids are reduced by sodium in presence of alcohol according to the equations: $R\cdot CO_2Et + 2H_2 = R\cdot CH_2\cdot OH + EtOH$ and $R\cdot CO_2Et + 4Na + 3EtOH = R\cdot CH_2\cdot OH + 4NaOEt$. The ester is dissolved in three to four times its weight of alcohol and slowly dropped on to 6 atomic proportions of sodium in a reflux apparatus. The rate of flow should be

such that the mixture keeps in active ebullition during the addition. After cooling, sufficient water is added to liquefy the whole, and the greater part of the ethyl alcohol is distilled off in a current of steam; the higher alcohol is extracted from the residue by ether and rectified. In this way, from methyl octoate, *n*-octyl alcohol has been obtained; at the same time, about 5 per cent. of the mixture is reduced, giving the bi-secondary glycol, $C_7H_{15}\cdot CH(OH)\cdot CH(OH)\cdot C_7H_{15}$, which boils at about 200° under a pressure of 10 mm. and crystallises when cooled. The *n*-octyl alcohol obtained boils at 96° under a pressure of 17 mm.

n-*Octyl acetate*, obtained from octyl alcohol and acetic anhydride, boils at 98° under a pressure of 15 mm.

Methyl n-*octyl ether*, produced by the action of methyl iodide on sodium octoxide, boils at 75° under a pressure of 20 mm.

By the action of *n*-octyl alcohol on carbanilide in light petroleum solution, n-*octylphenylurethane*, $C_7H_{15}\cdot CH_2\cdot O\cdot CO\cdot NHPh$, is formed. It crystallises from methyl alcohol and melts at 74°. J. McC.

Action of Phosphorus Trichloride on Glycerol. P. CARRÉ (*Compt. rend.*, 1903, 136, 1456—1458. Compare Abstr., 1902, i, 131 and 338, and Lumière and Perrin, *ibid.*, i, 9).—The author now shows that when phosphorus trichloride is added to anhydrous glycerol there are first formed the compounds $P_2O_6(C_3H_5)_2$ and $C_3H_5Cl{:}O_2{:}P\cdot OH$. The former, on treatment with water, is converted first into the substance $P_2(OH)_2({:}O_2{:}C_3H_5\cdot OH)_2$, and eventually into the acid ester, $P_2(OH)_4{:}O_2{:}C_3H_5\cdot OH$, which was isolated in the form of its deliquescent calcium salt. The second compound is converted into the substance $OH\cdot C_3H_5Cl\cdot O\cdot P(OH)_2$, of which the calcium salt was obtained in an impure form. T. A. H.

Pyrogenetic Contact Reactions of Organic Compounds. VII. Contact Metamerism. WLADIMIR IPATIEFF and W. LEONTOWITSCH (*Ber.*, 1903, 36, 2016—2019).—Ethylene oxide is completely converted into acetaldehyde by being slowly passed through a tube containing aluminium oxide and heated at 200°; propylene oxide, $\begin{matrix}CHMe\\|\\CH_2\end{matrix}\!\!>\!O$, under similar circumstances gives principally propaldehyde, but a small quantity of acetone is also formed; *iso*butylene oxide gives *iso*butaldehyde, and trimethylethylene oxide gives methyl *iso*propyl ketone, whilst methylethylethylene oxide, $\begin{matrix}CMeEt\\|\\CH_2\end{matrix}\!\!>\!O$, is converted into methylethylacetaldehyde.

When similar oxides are passed through glass tubes not containing the aluminium oxide, the transformation into ketone or aldehyde begins only at about 500°, and the products are then largely resolved into simpler substances. W. A. D.

Etherification with the Hydracids. ANTOINE VILLIERS (*Compt. rend.*, 1903, 136, 1551—1553).—The formation of ether from alcohol and hydrogen chloride takes place only to a small extent at 100°; at

the ordinary temperature, and even at 44°, no evidence could be found that it is formed at all. With hydrogen bromide or hydrogen iodide, its formation at 100° is abundant, and at 44° a good proportion is also produced.

In the absence of water, the hydracids may react on ether, but the action is stopped by even a small quantity of water.

Etherification completely ceases when a certain amount of water is present, and this is due to the formation of hydrates which do not act on the alcohol as the pure hydrogen chloride does. The limit of etherification is not independent of the temperature, for the dissociation of the hydrate of the acid by heating tends to increase the limit as the temperature rises. Further, the limits of etherification differ for the three hydracids because the dissociation of their hydrates is not the same.

The author intends to show that two initially identical systems may tend towards different equilibria according to the variations of temperature which they suffer before coming to the same final temperature.

J. McC.

Esterification of Sulphuric Acid. Antoine Villiers (*Compt. rend.*, 1903, **136**, 1452—1453. Compare Abstr., 1880, 796).—Esterification experiments, in which mixtures of ethyl alcohol and sulphuric acid have been allowed to remain at the ordinary temperature for a period of twenty-five years, show that the amount of ester formed is, under these conditions, 22·2 per cent., being equal to the amount found after 221 days at 44°, or after 154 hours at 100°. Since the maximum amount of ester producible is 29·5 per cent., retrogression must occur at the ordinary temperature, as has already been shown to be the case at higher temperatures. The results of experiments in which sulphuric acid containing water was used indicated, by comparison with the results of other determinations carried out at higher temperatures, that the retrogression under these conditions was only commencing at the end of twenty-five years at the ordinary temperature. T. A. H.

Preparation of Nitrous and Nitric Esters. Louis Bouveault and André R. Wahl (*Compt. rend.*, 1903, **136**, 1563—1564).—The nitric esters can be most conveniently prepared from real nitric acid (Franchimont) and the alcohol. The alcohol is slowly dropped into 3 parts of real nitric acid cooled to between 0° and 5°, the mixture is poured on to ice, and then extracted with ether. In this way, the following nitrates have been obtained. iso*Amyl nitrate* boils at 147—148°. n-*Octyl nitrate* boils at 110—112° under a pressure of 2 mm., and has a sp. gr. 0·975 at 4°/0°. n-*Decyl nitrate* is a colourless liquid, which boils at 127—128° under 11 mm. pressure and has a sp. gr. 0·951 at 4°/0°. *Myristyl nitrate* boils with slight decomposition at 175—180° under 12 mm. pressure, solidifies when cooled to 0°, and is only sparingly soluble in alcohol.

With secondary alcohols, real nitric acid only exerts an oxidising action, and with tertiary alcohols the action is so violent that a non-distillable product is formed.

Nitrous esters can be easily obtained by passing a current of

nitrosyl chloride into a molecular mixture of the alcohol and pyridine. n-*Octyl nitrite* boils at 174—175°. n-*Decyl nitrite* boils at 105—108° under 12 mm. pressure. sec.-*Octyl nitrite* boils at 65° under 15 mm. pressure.

The nitrites of primary alcohols have very different boiling points from the alcohols, for secondary alcohols the difference is less, and for tertiary alcohols it is insignificant. Consequently it is difficult to prepare the nitrites of tertiary alcohols in a pure state, although they are formed easily. Diethylpropylcarbinol boils at 160°, whilst its nitrite boils at 155°. J. McC.

Atmospheric Formic Acid. H. HENRIET (*Compt. rend.*, 1903, **136**, 1465—1467. Compare Abstr., 1902, i, 714).—The author has confirmed his previous observation that atmospheric air contains a neutral derivative of formic acid by isolating this acid from the liquid produced by condensing steam which had been diffused through large volumes of air. The same substance appears to be contained in the gases exhaled from soil. T. A. H.

Solubility of Normal and Acid Formates of the Alkalis. E. GROSCHUFF (*Ber.*, 1903, **36**, 1783—1795).—The formates of potassium, sodium, and lithium can be prepared in an anhydrous state, the potassium salt melts at 157°, the sodium salt at 253°, and the lithium salt decomposes before melting; the potassium and sodium salts are strongly hygroscopic.

Lithium formate crystallises with $1H_2O$ below 94°. Sodium formate crystallises with $2H_2O$ between 25° and 19° and with $3H_2O$ below 19°; the existence of a monohydrate and tetrahydrate could not be proved. The acid salt, HCO_2K,HCO_2H, decomposes at 95°, and the acid sodium salt, HCO_2Na,HCO_2H, at 66°, yielding formic acid and a normal salt. T. M. L.

Chlorine Derivatives of Methylene Chloroacetate and Diacetate. MARCEL DESCUDÉ (*Compt. rend.*, 1903, **136**, 1565—1566. Compare this vol., i, 232).—By the action of chloroacetyl chloride on the polymerisation product of formaldehyde in presence of zinc chloride, a mixture is obtained from which *chloromethyl chloroacetate*, $CH_2Cl·CO_2·CH_2Cl$, has been isolated by distillation in a vacuum. It is a colourless liquid with a strong odour, boils at 155—160° under atmospheric pressure and at 82—83° under 22 mm. pressure, has a sp. gr. 1·420 at 18°, and is easily soluble in the common organic solvents; water decomposes it slowly into hydrogen chloride, chloroacetic acid, and formaldehyde, and this decomposition is instantaneous in presence of alkali. When heated with alcohol for several hours, an analogous decomposition takes place, so that hydrogen chloride, chloroacetic acid, and diethylformal are produced. The residue of the distillation is a viscous liquid which crystallises after some time. It consists of *methylene chloroacetate*, $CH_2(CO_2·CH_2Cl)_2$, which separates from alcohol in white plates melting at 52—53°.

The action of trichloroacetyl chloride on formaldehyde is much

slower, but proceeds in the same way; *chloromethyl trichloroacetate*, $CCl_3 \cdot CO_2 \cdot CH_2Cl$, and *methylene trichloroacetate*, $CH_2(CO_2 \cdot CCl_3)_2$, have been obtained. The former boils at 170° and the latter crystallises from light petroleum and melts at 76°. J. McC.

New Plumbic Derivatives. Preparation. Thermochemical Study. ALBERT COLSON (*Compt. rend.*, 1903, 136, 1664—1666. Compare this vol., i, 396, 456).—Lead acetate and propionate dissolved in acetic or propionic acids are converted into plumbic salts by the action of chlorine; a similar action, however, does not take place so easily with the butyrates. When chlorine is passed into a solution of lead *iso*butyrate in *iso*butyric acid, about equal quantities of lead chloride and tetra*iso*butyrate are formed. After keeping for 24 hours, the liquid is filtered and on evaporation deposits crystals of *lead tetra*iso*butyrate*, $Pb(C_4H_7O_2)_4$, in octahedra which melt at 109°. The tetra-*n*-butyrate cannot be formed in this way, but if lead tetra-acetate is warmed on the water-bath under diminished pressure with excess of *n*-butyric acid, acetic acid is expelled and the *tetra*-n-*butyrate* is formed, which could not, however, be crystallised.

Lead tetrastearate, $Pb(C_{18}H_{35}O_2)_4$, can be produced from lead tetra-acetate and stearic acid. It is obtained as a white, crystalline substance, melts at 102—103°, and is rapidly decomposed by alcohol or dilute solutions of alkalis, but only slowly by water, which does not moisten it. *Lead tetrapalmitate*, $Pb(C_{16}H_{31}O_2)_4$, formed in the same way, melts at 88—91°.

The heats of decomposition of the tetra-acetate and tetrapropionate are: $Pb(C_2H_3O_2)_4$ (solid) + Aq. = PbO_2, nH_2O + $4C_2H_4O_2$ (dissolved) − 2·75 Cal.; $Pb(C_3H_5O_2)_4$ (solid) + Aq. = PbO_2, nH_2O + $4C_3H_6O_2$ (dissolved) − 4·9 Cal. The temperature changes which follow the dissolution of these substances in water indicate that physical solution first takes place with lowering of temperature, then decomposition with development of heat takes place.

The heat of solution of lead tetra-acetate in acetic acid is − 3·85 Cal. J. McC.

Acetylchromic Acid. AMÉ PICTET and P. GENEQUAND (*Ber.*, 1903, 36, 2215—2219).—Acetylchromic acid, $OH \cdot CrO_2 \cdot OAc$ (compare this vol., i, 456), is a less powerful oxidising agent than chromic acid, dissolving quietly in ethyl or methyl alcohol, oxidation only commencing after a time. When the solid acid is moistened with alcohol or acetone, ignition does not occur. A cryoscopic determination in glacial acetic acid solution gave the molecular weight 233, indicating combination with a further molecule of acetic acid. This was also found to be the case with diacetylorthonitric acid (compare Abstr., 1902, i, 584). *Butyrochromic acid*, $OH \cdot CrO_2 \cdot C_4H_7O_2$, is very similar in properties. Formic and valeric acids are oxidised so readily by chromic acid that similar compounds could not be prepared.

C. H. D.

Mixed Anhydrides of Boric Acid and Organic Acids. AMÉ PICTET and ANTONINE GELEZNOFF (*Ber.*, 1903, 36, 2219—2225).—Triacetic boric anhydride crystallises in colourless needles melting at

121° (compare this vol., i, 309) and dissolves in chloroform, acetone, ethyl acetate, or glacial acetic acid, but not in ether, light petroleum, or carbon tetrachloride. Its molecular weight, determined cryoscopically in glacial acetic acid solution, is normal. It reacts on warming with many organic acids, acetic acid being set free and a new mixed anhydride being formed. The same compounds are obtained by the action of acyl chlorides or acid anhydrides on boric acid.

Tri-trichloroaceticboric anhydride, $(CCl_3\cdot CO_2)_3B$, separates from acetone in colourless crystals melting at 165°; *tri-n-butyric boric anhydride*, $(C_3H_7O_2)_3B$, is a liquid with the sp. gr. 1·064 at 23°; *triisovaleric boric anhydride*, $(C_5H_9O_2)_3B$, is liquid, sp. gr. 1·024 at 21·5°; *tristearic boric anhydride*, $(C_{18}H_{35}O_2)_3B$, forms small, white crystals melting at 73°; *trisuccinic boric anhydride*, $(C_4H_4O_4)_3B_2$, melts at 164°; *tribenzoic boric anhydride*, $(C_6H_5\cdot CO_2)_3B$, crystallises from benzene in flattened needles melting at 145°; *trisalicylic boric anhydride*, $(C_7H_5O_3)_3B$, forms microscopic needles melting at 258—259°, insoluble in all organic solvents, except benzene, and *triphthalic boric anhydride*, $(C_8H_4O_4)_3B_2$, crystallises from acetone or chloroform in prismatic needles melting at 165°.

C. H. D.

Propolis. MAURITS GRESHOFF and J. SACK (*Rec. trav. chim.*, 1903, 22, 139—142).—Propolis is a wax which is collected by bees from the resinous shoots of several trees, and has a dirty greyish-brown colour; it has an aromatic odour, melts at about 64°, has a sp. gr. 1·2, and is completely soluble in boiling 95 per cent. alcohol. On cooling, a *wax* (12 per cent.) separates which consists of a mixture of cerotic acid and an ester of melissyl alcohol; the resinous portion soluble in alcohol, which forms 84 per cent. of the original product, after suitable purification melts at 66°, has the composition $C_{26}H_{26}O_8$, and on boiling with acetic anhydride gives a triacetate, $C_{26}H_{23}O_8(OAc)_3$.

W. A. D.

Rare Oils. J. J. A. WIJS (*Zeit. Nahr.-Genussm.*, 1903, 6, 492—496). —The chemical and physical constants of the following oils are given:

	Sp. gr. at 20°/4°.	Free acid (as oleic). Per cent.	Iodine number.	Saponification number.
Echinops oil (2 samples) ...	0·9285—0·9253	4·38—7·31	138·1—141·2	189·2—190·0
Perilla oil (Japanese)	0·9306	0·48	206·1	189·6
Water-melon seed oil	0·9160	1·20	118·0	189·7
Tea seed oil (Japanese)......	0·9110	8·07	88·9	188·3
Cress seed oil (pressed)......	0·9212	0·56	133·4	186·4

The fatty acids separated from these oils gave the following figures:

	Melting point.	Acid number.	Mean molecular weight.	Iodine number.
Fatty acids from echinops oil ...	11—12°	192·3—192·9	292—291	139·1—143·8
,, ,, perilla oil......	–5	197·7	284	210·6
,, ,, water-melon seed oil......	34	197·1	284·1	122·7
,, ,, tea seed oil ...	10—11	195·9	286	90·8
,, ,, cress seed oil...	—	193·0	291	137·7

The iodine numbers were estimated by the iodine monochloride method. None of the oils gave colorations with Halphen's or Baudouin's reagents. W. P. S.

Nitric Esters of Hydroxy-acids. H. DUVAL (*Bull. Soc. chim.*, 1903, [iii], 29, 601—603).—*Glycollic acid nitrate*, $NO_2·O·CH_2·CO_2H$, prepared by solution of glycollic acid in a mixture of nitric and sulphuric acids and purification of the crude ester by extraction with benzene containing ten per cent. of light petroleum, crystallises in colourless, deliquescent prisms, melts at 54·5°, and is soluble in water, alcohol, ether, or benzene, but not in light petroleum. T. A. H.

Compounds of Ethyl Acetoacetate and Acetylacetone with Metallic Chlorides. ARTHUR ROSENHEIM, WILLY LOEWENSTAMM, and LUDWIG SINGER (*Ber.*, 1903, 36, 1833—1839. Compare W. Dilthey).—When silicon tetrachloride and ethyl acetoacetate, both in ethereal solution, are mixed, a compound, $Si(CHAc·CO_2Et)_3Cl,HCl$, is obtained, which crystallises in prisms melting and decomposing at 96—98° and soluble in dry chloroform.

Titanium tetrachloride forms, with acetylacetone in ethereal solution, deep red prisms which contain a molecule of ether,

$$TiCl_3·CH(COMe)_2,Et_2O.$$

When crystallised from other solvents, a yellow, crystalline, hygroscopic substance is obtained. Ethyl acetoacetate forms a similar compound, $TiCl_3{:}CAc·CO_2Et,Et_2O$, which crystallises from ether in deep red rhombs or from other solvents as a yellow, hygroscopic compound. In chloroform solution, the first product of the interaction with acetylacetone is a yellow compound, probably $C_5H_8O_2,TiCl_4$, which, however, at once loses hydrogen chloride.

Tin tetrachloride forms a similar, very unstable, intermediate compound, which at once loses hydrogen chloride and forms

$$Sn(C_5H_7O_2)_2Cl_2.$$

Ethyl acetoacetate in cold ethereal solution gives a snow-white, crystalline substance, $C_6H_{10}O_3,SnCl_4$. When heated in chloroform solution, hydrogen chloride is evolved and a compound, $2C_6H_{10}O_3,3H_2SnCl_6$, crystallising in white plates is obtained.

Antimony pentachloride combines with acetylacetone dissolved in carbon tetrachloride to form slender, yellow needles of the composition $C_5H_8O_2,SbCl_5$; these lose hydrogen chloride when exposed to the atmosphere. In chloroform solution, after boiling to expel all hydrogen chloride, a stable compound, $SbCl_4 \cdot C_5H_7O_2$, is formed; this crystallises in yellow prisms melting at 127°. Benzoylacetone forms a similar molecular compound, $C_{10}H_{10}O_2,SbCl_5$, crystallising in yellow needles. Ethyl acetoacetate in cold ethereal solution forms a very unstable, colourless, additive compound, $C_6H_{10}O_3,HSbCl_6$. In chloroform solution, yellow, prismatic crystals are obtained, which lose hydrogen chloride to form a substance having the complicated composition $C_6H_{10}O_3,SbCl_5,2HSbCl_6$.

Platinum tetrachloride yields an additive compound with acetylacetone, $PtCl_2(C_5H_7O_2)_2,HCl$, which crystallises in purple-red needles, insoluble in most solvents. Boron trichloride gives compounds externally similar to those of silicon. E. F. A.

α-*iso*Propyl- and α-Dimethyl-β-hydroxybutyric Acids. ALFRED WOGRINZ (*Monatsh.*, 1903, **24**, 245—250. Compare Abstr., 1901, i, 254).—Reduction of ethyl *iso*propylacetoacetate by sodium amalgam in aqueous alcoholic solution leads to the formation of *β-hydroxy-α-*iso*propylbutyric acid*, $OH \cdot CHMe \cdot CHPr^{\beta} \cdot CO_2H$, which is a thick, colourless syrup and boils at 144—148° under 12—15 mm. and at 160—165° under 30—35 mm. pressure, and distils, almost without decomposition, at 250° under the ordinary pressure. This acid is identical with the acid obtained on oxidation of the aldol formed from *iso*valeraldehyde and acetaldehyde. The aldol has the constitutional formula, $CHMe_2 \cdot CH(CHO) \cdot CHMe \cdot OH$. *β-Hydroxy-α-dimethylbutyric acid*, formed by reduction of ethyl dimethylacetoacetate, is a thick, clear syrup, boils at 143—145° under 15—16 mm. and at 150° under 22 mm. pressure, cannot be crystallised, is easily soluble in water, alcohol, or ether, and partly decomposes with formation of acetaldehyde when boiled in a reflux apparatus. This acid is identical with Lilienfeld and Tauss' hydroxy-acid (Abstr., 1898, i, 509). Braun's β-hydroxy*iso*hexoic acid (β-hydroxy-γ-dimethylbutyric acid) distils unchanged at 165—166° under 35 mm. and at 173—175° under 43 mm. pressure (Abstr., 1896, i, 595). G. Y.

Synthesis of αα-Dimethylglutaric Acid. EDMOND E. BLAISE (*Compt. rend.*, 1903, **136**, 1463—1465. Compare Abstr., 1902, i, 530, this vol., i, 315, 316, and 400, and Perkin and Smith, Trans., 1903, **83**, 8).—αα-Dimethylglutaconic acid is converted by hydriodic acid into *β-iodo-αα-dimethylglutaric acid*, which crystallises from ether on addition of light petroleum and melts and decomposes at 168°. It is decomposed by ebullition with water into dimethylvinylacetic acid, $CO_2H \cdot CMe_2 \cdot CH{:}CH_2$ (Perkin, Trans., 1902, **81**, 256), and the corresponding *lactone*. The former has an odour like that of hexoic acid, boils at 111—112° under 22 mm. pressure, and yields an *anilide*, which crystallises in prismatic needles and melts at 106°; the lactone, also producible by the action of sulphuric acid on dimethylvinylacetic acid, is a colourless liquid which boils at 202—203°.

$\alpha\alpha$-Dimethylglutaric acid was obtained by reducing iododimethylglutaric acid with zinc and sulphuric acid; it melts at 84° (compare Perkin and Smith, *loc. cit.*). T. A. H.

Electrolytic Reduction of Unsaturated Acids. CH. MARIE (*Compt. rend.*, 1903, **136**, 1331—1332).—When a solution of aconitic acid, to which half the quantity of sodium hydroxide necessary for complete neutralisation has been added, is electrolytically reduced, using a cathode of mercury and an anode of platinum, and an apparatus (described in the original) designed to prevent, as far as possible, oxidation at the anode, a yield of 60 per cent. of the theoretical quantity of tricarballylic acid can be obtained. The acids were separated by conversion into their copper salts, that of aconitic acid being soluble in dilute acetic acid.

Cinnamic acid can by this method be converted quantitatively into phenylpropionic acid. T. A. H.

Action of Hydrogen Sulphide on Methyl Ethyl Ketone. F. LETEUR (*Compt. rend.*, 1903, **136**, 1459—1460).—When methyl ethyl ketone, previously saturated with hydrogen chloride at $-28°$ to $-30°$, is treated at the same temperature with dry hydrogen sulphide (compare Fromm and Baumann, Abstr., 1889, 152), there is formed the compound $(C_4H_8S)_3$, which is a polymeride of butanethione. This, when freed from an associated impurity of repulsive odour, is a limpid, amber-coloured oil of slight alliaceous odour; it decomposes when heated under atmospheric pressure, but boils at 238° under 175 mm. pressure, does not solidify at $-25°$, is soluble in organic liquids but insoluble in water, and inflames on addition of nitric acid.

T. A. H.

Oxidation by means of Ozone. CARL D. HARRIES (*Ber.*, 1903, **36**, 1933—1936).—A yellow oil, probably a peroxide,

$$CMe_2{<}{}^{O}_{O}{>}CHAc,$$

is formed when ozone is passed into well cooled mesityl oxide. When removed from the freezing mixture, it decomposes with explosive violence. When the oxide is treated with ozone in the presence of water, the products are acetone and methylglyoxal, presumably obtained by the decomposition of the peroxide.

Methylheptenone, under similar treatment, yields acetone and pentanolal (lævulinaldehyde) (Abstr., 1898, i, 232). Allylacetone also yields pentanonal. Unsaturated aldehydes behave in a similar manner, for example: acralacetal, $CH_2{:}CH{\cdot}CH(OEt)_2$, yields the *half acetal of glyoxal*, $CHO{\cdot}CH(OEt)_2$, distilling at 80—90° under atmospheric pressure. Maleic acid yields glyoxylic acid. Methyl fumarate yields a small amount of methyl glyoxylate, the *phenylhydrazone* of which melts at 139°. Cinnamic acid yields benzaldehyde and glyoxylic acid. Methyl alcohol yields formaldehyde and glycerol yields glyceraldehyde.

J. J. S.

Acetyltrimethylene. CARL D. HARRIES (*Ber.*, 1903, **36**, 1795—1797).—Controversial, in reply to Scheda (this vol., i, 509).
T. M. L.

Reactions of Pinacolin and Pinacone. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1903, [iii], **29**, 597—601).—The author has shown that ketones containing the acetyl group and therefore having the carbonyl attached to a hydrocarbon residue form additive compounds with mercuric sulphate (Abstr., 1899, ii, 256) and give Legal's colour reaction (Abstr., 1897, ii, 467). In conformity with this observation, pinacolin gives a yellow, crystalline, additive compound with mercuric sulphate, a carmine-red coloration with Legal's test (*loc. cit.*), furnishes iodoform with iodine and alkali hydroxides, and bromoform with sodium hypobromite. Pinacone, on the contrary, does not give these reactions, although under certain conditions it is oxidised by sodium hypobromite to tribromoacetone with the ultimate formation of bromoform. The conditions under which these reactions may be applied to the detection of pinacolin are described in the original. T. A. H.

Zinc Compound of Dextrose. ANTON VON GRABOWSKI (D.R.-P. 139954).—A zinc compound of dextrose, $Zn(OH)_2 \cdot C_6H_{12}O_6$, may be prepared by addition of a solution of a zinc salt to dextrose-syrup and neutralisation with alkali. The compound dissolves in water to a clear solution, and so differs from Chapman's compound,

$$2ZnO,C_6H_{12}O_6,3H_2O,$$

which is decomposed by water (Trans., 1889, **55**, 576). C. H. D.

Stachyose. CHARLES TANRET (*Compt. rend.*, 1903, **136**, 1569—1571. Compare von Planta and Schulze, Abstr., 1890, 1088; 1891, 1446; 1902, i, 594; Tanret, Abstr., 1902, i, 661).—When stachyose is hydrolysed with 3 per cent sulphuric acid, it gives 4 mols. of monoses namely, 2 mols. of galactose, 1 mol. of dextrose, and 1 mol. of lævulose; when hydrolysed by acetic acid, it gives 1 mol. of lævulose and 1 mol. of a triose, and on hydrolysing this triose with sulphuric acid 2 mols. of galactose and 1 mol. of dextrose are obtained. These facts show that stachyose is a tetrose.

Comparison of the chemical and physical properties of stachyose and manneotetrose (Tanret, *loc. cit.*) prove that they are identical.
J. McC.

Ammonium Magnesium Arsenates. Methylammonium and Trimethylammonium Magnesium Arsenates. M. BRISAC (*Bull. Soc. chim.*, 1903, [iii], **29**, 591—592).—The addition of methylamine, in excess, to a solution of sodium hydrogen arsenate in dilute hydrochloric acid, followed by a solution of magnesium sulphate, results in the precipitation of *magnesium methylammonium arsenate*,

$$NH_3Me \cdot MgAsO_4,8H_2O,$$

as a white, crystalline powder.

Magnesium trimethylammonium arsenate, $NHMe_3 \cdot MgAsO_4,6H_2O$, prepared in similar manner, closely resembles the foregoing salt in appearance. T. A. H.

Methylammonium and Trimethylammonium Magnesium Phosphates. CH. PORCHER and M. BRISAC (*Bull. Soc. Chim.*, 1903, [iii], 29, 587—591).—*Methylammonium magnesium phosphate* (with $6H_2O$) and *trimethylammonium magnesium phosphate* (with $4H_2O$) are prepared by mixing the hydrochlorides of the amines with a slight excess of 10—15 per cent. solutions of disodium phosphate. On adding a solution of magnesium sulphate, a slight crystalline precipitate is formed. This is dissolved by two or three drops of hydrochloric acid. The free base is then added drop by drop until the solution is strongly alkaline. Another method is to gradually add magnesium sulphate to a strongly alkaline mixture of the hydrochloride of the base and sodium phosphate. N. H. J. M.

Formaldehyde Derivatives of Urethanes. MAX CONRAD and KARL HOCK (*Ber.*, 1903, 36, 2206—2208).—*Methylenediurethane*, $CH_2(NH \cdot CO_2Et)_2$, prepared by condensing urethane (2 mols.) with formaldehyde (1 mol.) in presence of hydrochloric acid, crystallises from alcohol or benzene, melts at 131°, is tasteless, and sparingly soluble in water, readily so in alcohol or ether. The corresponding *compound* from methylurethane melts at 125°, but was not further investigated.

Anhydroformaldehydeurethane has been obtained in small quantity by Bischoff and Reinfeld (this vol., i, 233). It may be prepared from urethane (1 mol.), formaldehyde (1 mol.), and hydrochloric acid. The temperature rises to 70—80°, and the reaction is completed by heating in a reflux apparatus. The viscous oil so obtained is extracted with ether, dehydrated by heating, and caused to crystallise by heating with acetic anhydride. The product crystallises from alcohol, melts at 102°, dissolves readily in cold benzene, and is intensely bitter. A molecular weight determination by Beckmann's method shows the molecule to be doubled, and a ring is probably present, $CO_2Et \cdot N<{CH_2 \atop CH_2}>N \cdot CO_2Et$. Both compounds are non-poisonous, but exhibit no specific physiological action. C. H. D.

Separation of Glycine and its Homologues from Inorganic Compounds. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 141976).—In the preparation of glycine, the product is obtained mixed with inorganic salts, from which it is separated by the troublesome method of conversion into the copper salt. This may be avoided by extracting the mass with glycerol at 100—150° and removing the glycerol by distillation in a vacuum or with steam, or by precipitating the glycine from the glycerol solution with ethyl or methyl alcohol. For many purposes, such as the preparation of phenylglycine-*o*-carboxylic acid, the solution in glycerol may be employed directly. C. H. D.

Synthesis of some Dipeptide Derivatives. EMIL FISCHER and ERICH OTTO (*Ber.*, 1903, 36, 2106—2116. Compare this vol., i, 465). —The methods used to synthesise polypeptides are also applicable to the carbethoxy-derivatives of the simple amino-acids.

Carbethoxyglycine ester, $CO_2Et\cdot NH\cdot CH_2\cdot CO_2Et$, produced by the combination of glycine ester and ethyl chlorocarbonate in presence of alkali, is a colourless oil boiling at 135° under 16 mm. pressure, or at 126° under 12 mm., and crystallises in monoclinic prisms melting at 27—28° (corr.), which are easily soluble in organic solvents and in about 10 parts of water. Alkali hydroxides hydrolyse this to *carbethoxyglycine*, which crystallises in prisms melting at 75° (corr.), reacts and tastes acid, and gives characteristic precipitates with metallic salts. It is obtained directly from glycine ester when more alkali is used, with a yield of 78 per cent.

Carbethoxyglycinamide, $CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, prepared by the action of liquid ammonia on the ester, crystallises in thin plates which sinter at 95° and melt at 101—103·5° (corr.).

Carbethoxyglycine chloride, prepared by the action of thionyl chloride on carbethoxyglycine, cannot be distilled without decomposition, and does not crystallise; water or alcohol reconvert it into the glycine or glycine ester. It combines easily with glycine ester to form carbethoxyglycylglycine ester and with glycylglycine ester to form carbethoxydiglycylglycine ester, a yield of 90 per cent. being obtained in the latter case. This method of preparation is thus to be preferred to that previously described. Similarly, the chloride combines with alanine ester to form *carbethoxyglycylalanine ester*,

$$CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2Et,$$

which forms star-shaped aggregates of small needles, sinters at 62°, and melts at 65·5—66·5° (corr.).

Liquid ammonia converts it into *carbethoxyglycylalanineamide*, melting at 136·5—137·5° (corr.) and showing a marked red violet biuret reaction.

Carbethoxyglycylalanine, formed from the ester by hydrolysis with normal sodium hydroxide, crystallises in long needles melting at 187·5—188·5° (corr.).

Chloroacetylalanine ester, $CH_2Cl\cdot CO\cdot NH\cdot CHMe\cdot CO_2Et$, prepared by the direct combination of chloroacetyl chloride and alanine ester in cold ethereal solution, crystallises in long needles or plates with pyramidal faces melting at 48·5—49·5° (corr.). It is soluble in about 15 parts of water, easily so in most organic solvents except light petroleum, and loses chlorine on boiling with alkali, forming *glycine-alanine-anhydride* or *methyldiketopiperazine*, $NH{<}\substack{CH_2—CO\\ CO\cdot CHMe}{>}NH$. This crystallises in needles, becomes brown at 236°, and melts and decomposes at 244—245° (corr.).

Chloroacetylglycylglycine ester, similarly formed by the combination of chloroacetyl chloride and glycylglycine ester in chloroform solution, crystallises in needles melting at 153—154° (corr.), and, on hydrolysis, yields *chloroacetylglycylglycine* crystallising from water in prisms melting at 178—180° (corr.). This, on heating with aqueous ammonia, yields a crystalline compound free from chlorine, which is in all probability a tripeptide, *diglycylglycine*, $NH_2\cdot[CH_2\cdot CO\cdot NH]_2\cdot CH_2\cdot CO_2H$.

Acetylalanine, $CH_3\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, prepared by the action of acetic anhydride on alanine (Abstr., 1901, i, 192), crystallises from acetone in rhombic plates melting at 137°.

Acetylglycylglycine, prepared by hydrolysing glycylglycine ester with normal alkali (Abstr., 1902, i, 350), melts at 187—189° (corr.).

E. F. A.

Action of Potassium Selenocyanate on Compounds of Chloroacetic Acid. HEINRICH FRERICHS (*Arch. Pharm.*, 1903, **241**, 177—222. For analogous thio-derivatives, compare Abstr., 1900, i, 478; 1902, i, 763).—Potassium selenocyanate was prepared by Muthmann and Schröder's method (Abstr., 1900, i, 479) and used in the form of a 10 per cent. alcoholic solution. The solution, as obtained directly, was found to contain a little potassium carbonate, which influenced the yields unfavourably; better yields were obtained when a few drops of hydrochloric acid were added to the alcoholic solution before using it. This solution was heated with various compounds of the type $CRO \cdot NH \cdot CO \cdot CH_2Cl$, namely, chloroacetylcarbamide, chloroacetylmethylcarbamide, chloroacetylphenylcarbamide, and ethyl chloroacetylcarbamate [$R = NH_2$, NHMe, NHPh, and OEt respectively], and with chloroacetamide, $NH_2 \cdot CO \cdot CH_2Cl$, and α-bromopropionylcarbamide, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CHMeBr$. It is doubtful whether the product has the constitution $CRO \cdot NH \cdot CO \cdot CH_2 \cdot SeCN$ or $CRO \cdot NH \cdot CO \cdot CH_2 \cdot NCSe$, for whilst, on the one hand, aqueous sodium hydroxide causes the formation of sodium cyanide, on the other, heating, either alone or with water, aniline, or toluidine, gives rise as a rule to a diselenoglycolyl compound of the type $Se_2(CH_2 \cdot CO \cdot NH \cdot CRO)_2$. The numbers given below are melting points, decomposition often occurring along with the melting.

Selenoacetocyanocarbamide, $R = NH_2$, 178—179°, yields *diselenoglycolylcarbamide*, 221°, when boiled with water, and hydantoin, $CO<\begin{matrix} NH \cdot CO \\ NH \cdot CH_2 \end{matrix}$, along with ammonium selenocyanate and a little of the diseleno-derivative when boiled with 10 per cent. ammonia (selenocyanoacetocarbamide will also exchange its SeCN group for SO_2Ph and NCS when heated in alcoholic solution with sodium benzenesulphinate and potassium thiocyanate respectively; in the latter case, an immediate transformation of the product into thiohydantoin occurs). *Selenocyanoacetomethylcarbamide*, R = NHMe, 148—149°, yields *diselenoglycolylmethylcarbamide*, 183—184°, when heated with water or aniline. *Selenocyanoacetophenylcarbamide*, R = NHPh, 147—148°, yields diphenylcarbamide and *selenohydantoin*,

$$NH:C<\begin{matrix} NH \cdot CO \\ Se - CH_2 \end{matrix},$$

190°, when boiled with water, in this respect resembling the thio- rather than the seleno-compounds. Ethyl selenocyanoacetocarbamate, R = OEt, could only be obtained as an oil, and would not form a hydantoin derivative. *Selenocyanoacetamide*, $NH_2 \cdot CO \cdot CH_2 \cdot SeCN$, 123—124°, would not form a diseleno-derivative. *α-Selenocyanopropionylcarbamide*, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CHMe \cdot SeCN$, 136°, yields *α-methylselenohydantoin*, $NH:C<\begin{matrix} NH \cdot CO \\ Se - CHMe \end{matrix}$, 179°, when boiled with ammonia.

The reaction of potassium selenocyanate with many substances of the type $NHR \cdot CO \cdot CH_2Cl$ was investigated. The product,

$$NHR \cdot CO \cdot CH_2 \cdot SeCN,$$

when heated with strong hydrochloric acid, and sometimes glacial acetic acid as well, yielded a diselenoglycollo-derivative,

$$Se_2(CH_2 \cdot CO \cdot NHR)_2.$$

Some carbamidoselenoglycollo-derivative, $NHR \cdot CO \cdot CH_2 \cdot Se \cdot CO \cdot NH_2$, was probably formed at the same time; it was seldom possible to isolate it, however, but on acidifying the solution a smell of cyanic acid was apparent, and on adding ammoniacal copper sulphate solution a precipitate of $(NHR \cdot CO \cdot CH_2 \cdot Se)_2Cu_2$ was obtained.

Selenocyanoacetanilide, R = Ph, 129°; *diselenoglycolloanilide*, 158°; *carbamidoselenoglycolloanilide* (impure), 118—119°; *cuproselenoglycolloanilide*. *Selenocyanoacetotoluidides*, $R = C_6H_4Me$: *o*, 126°; *m*, 136°; *p*, 160°; *diselenoglycollotoluidides*: *o*, 174—175°; *m*, 158°; *p*, 174°. *Selenocyanoaceto-xylidides*, $R = C_6H_3Me_2$: *m* (asymm.), 148°; *p*, 144—146°; *diselenoglycollo-xylidides*: *m*, (asymm.), 184°; *p*, 180—181°. *Selenocyanoacetochloroanilides*, $R = C_6H_4Cl$: *m*, 117—118°; *p*, 178°; *diselenoglycollo*-m-*chloroanilide*, 183°. *Selenocyanoacetobromoanilides*, $R = C_6H_4Br$: *m*, 105°; *p*, 188°; *diselenoglycollo*-m-*bromoanilide*, 198°. *Selenocyanoacetoanisidides*, $R = C_6H_4 \cdot OMe$: *o*, 110°; *p*, 131°; *diselenoglycollaniside*; *o*, 124°; *p*, 172°.

Some compounds were prepared in which the NHR group is replaced by NPhR: *Selenocyanoacetomethylanilide*, R = Me, 78°; *diselenoglycollomethylanilide*, 94—95°; *carbamidoselenoglycollomethylanilide*, 123°; *cuproselenoglycollomethylanilide*. *Selenocyanoacetobenzylanilide*, $R = CH_2Ph$, 70°; *diselenoglycollobenzylanilide*, 81°; *carbamidoselenoglycollobenzylanilide*, 140—141°; *cuproselenoglycollobenzylanilide*. *Selenocyanoacetodiphenylamide*, R = Ph, 103°; *diselenoglycollodiphenylamide*, 123—124°.

Chloroacetobromoanilides, $C_6H_4Br \cdot NH \cdot CO \cdot CH_2Cl$, were obtained by mixing chloroacetylchloride with bromoaniline in benzene solution: *m*, 114°; *p*, 179°. In a similar manner, *chloroacetobenzylanilide*,

$$CH_2Ph \cdot NPh \cdot CO \cdot CH_2Cl,$$

80—81°, and *chloroacetodiphenylamide*, $NPh_2 \cdot CO \cdot CH_2Cl$, 118°, were prepared from benzylaniline and diphenylamine respectively.

C. F. B.

Behaviour of Tertiary Nitrogen Derivatives with a Negative Grouping towards Cyanogen Bromide. JULIUS VON BRAUN (*Ber.*, 1903, 36, 2286—2290).—When cyanogen bromide acts on tertiary bases, an unstable derivative of quinquevalent nitrogen is probably formed as an intermediate product, thus: $NR_3Br \cdot CN = NR_2 \cdot CN + BrR$ (von Braun, Abstr., 1900, i, 430). The author has now investigated the action of cyanogen bromide on tertiary nitrogen derivatives, where one of the valencies of the latter is saturated by a negative grouping and the two other valencies by positive groupings.

Compounds with the groupings $-COR$, $-COH$, $-SO_2Ph$ (acid amides, benzenesulphonamides), and $-CO_2R$ (urethanes) do not interact with cyanogen bromide either in the cold or when heated. Compounds with the groupings $-NO$ (nitroso-compounds), $-CN$ (cyanoamides),

–CSSR (dithiourethanes), compounds of the type of the dithioamine, $R_2N–S–S–NR_2$, chloroamines, R_2NCl, and derivatives of hydroxylamine interact with cyanogen bromide with more or less ease. Nitrosoamines, cyanoamides and dithiourethanes are not attacked in the cold, but resinify slightly on being heated. Nitrogen derivatives, on the other hand, containing chlorine or hydroxyl groups, are very readily attacked.

Dipropylformamide, prepared by distillation of dipropylamine-hydrochloride with sodium formate, is a colourless, inodorous liquid which boils at 202—204°.

Diethylpropionamide, prepared from diethylamine and propionyl-chloride, boils at 191°. *Diethylurethane*, prepared from diethylamine and ethyl chlorocarbonate, boils at 167°.

Dipropylurethane, prepared from dipropylamine and ethyl chlorocarbonate, boils at 97° under 20 mm. pressure. *Dibenzylurethane* is a viscid oil boiling at 216° under 28 mm. pressure. These compounds were all recovered unchanged after having been heated with cyanogen bromide in a closed vessel at 100°.

Dithiodiethylamine, $S_2(NEt_2)_2$, is acted on by cyanogen bromide at the ordinary temperature, and diethylamine hydrobromide was detected in the product. Diphenyl- and dipiperidyl-chloroamines are also readily attacked by cyanogen bromide. *Dipropylhydroxylamine* is acted on by cyanogen bromide with development of a considerable amount of heat, whilst *dibenzylhydroxylamine* melts to an amorphous mass with abundant evolution of benzaldehyde. When the action of dibenzylhydroxylamine on cyanogen bromide was conducted in ethereal solution, benzylamine hydrobromide and a substance melting at 115° and having the constitution $C_{20}H_{20}O_2N_4$ were isolated. A. McK.

A New Starting Material (Calcium Cyanamide) for the Preparation of Alkali Cyanides. GEORG ERLWEIN (*Zeit. angew. Chem.*, 1903, **16**, 533—536).—The author shortly reviews the methods which have been used for the production of cyanides from atmospheric nitrogen. A considerable advantage was gained by using calcium carbide in place of barium carbide in the preparation. The method now used consists in heating calcium carbide in nitrogen. The nitrogen does not unite directly with the carbide to produce cyanide, but there is a separation of carbon, and calcium cyanamide is formed: $CaC_2 + N_2 = CaCN_2 + C$. Calcium cyanamide is also formed when calcium oxide and carbon are heated in a resistance furnace in nitrogen: $CaO + 2C + N_2 = CaCN_2 + CO$. When treated with water, it decomposes into calcium hydroxide and dicyanodiamide: $2CaCN_2 + 4H_2O = 2Ca(OH)_2 + (CN{\cdot}NH_2)_2$. This can be isolated in a well-crystallised form resembling ammonium chloride. It is then fused with sodium carbonate and carbon, when the principal reaction which takes place is expressed by the equation $2C_2N_2(NH_2)_2 + 2Na_2CO_3 + 4C = 4NaCN + 2NH_3 + H_2 + 6CO + N_2$; but other reactions also take place, and some volatile products are obtained such as melamine. The cyanide formed is a pure white, crystalline product, and requires no purification. The ammonia is absorbed in sulphuric acid.

A product containing 30 per cent. of sodium cyanide is formed when

calcium cyanamide is fused with sodium chloride, and as this is cheaply produced it may have great technical value in gold extraction.

Dicyanodiamide may prove useful in the synthesis of carbamide derivatives. J. McC.

Compounds of Hydroferrocyanic Acid with Organic Substances. Paul Chrétien and Joseph Guinchant (*Compt. rend.*, 1903, 136, 1673—1675).—Hydroferrocyanic acid absorbs ether vapour to an extent which varies with the temperature. The dry acid was placed along with ether under a bell-jar and the increase in weight was determined. After exposure for 15 to 20 hours, the maximum quantity of ether had been absorbed; one molecule of acid absorbing at 0°, 2·71, at 8°, 2·61, at 16°, 2·45, and at 22°, 2·35 molecules of ether. The ether is only absorbed provided that moisture is present. The dissociation pressure of the mixture has been determined, and from the results it is deduced that a definite compound of 1 molecule of hydroferrocyanic acid and 2 molecules of ether is formed (compare Etard and Bémond, Abstr., 1885, 233; Browning, Trans., 1900, 77, 1233; Baeyer and Villiger, Abstr., 1902, i, 356), and the compound can absorb 0·71 molecule of ether at 0° to give a solid solution.

When perfectly dry, the compound is very stable, but in moist air it loses ether.

Hydroferrocyanic acid can absorb in the same way the vapour of acetone, ethylene oxide, epichlorohydrin, and allyl alcohol. The compound with allyl alcohol forms good crystals containing 4 molecules of the alcohol to 1 of acid. J. McC.

Potassium Vanadiocyanide. Emil Petersen (*Ber.*, 1903, 36, 1911).—*Potassium vanadiocyanide*, $K_4V(CN)_6,3H_2O$, obtained by reducing a solution of vanadium trihydroxide in acetic acid with potassium amalgam, adding potassium cyanide, and precipitating with alcohol, forms brownish-yellow, apparently tetragonal prisms and is very susceptible to oxidation. W. A. D.

Preparation of the Nitriles of Hydroxy-acids from Ketones. Hans Bucherer (D.R.-P. 141509).—Hydroxy-acid nitriles are conveniently prepared by treating the sodium hydrogen sulphite compounds of ketones with potassium cyanide (compare Abstr., 1902, i, 533). The patent describes the preparation of α-hydroxy*iso*butyronitrile, $OH\cdot CMe_2\cdot CN$, from acetone, of *ethyl β-cyanohydroxybutyrate*,

$$OH\cdot CMe(CN)\cdot CH_2\cdot CO_2Et,$$

from ethyl acetoacetate, and of a mixture of nitriles from the so-called "acetone oil." C. H. D.

Action of Carbamide and Thiocarbamide on Chromium Chloride Dihydrate. Paul Pfeiffer (*Ber.*, 1903, 36, 1926—1929).—Sell's hexacarbamidochromic salts (compare Werner and Kalkmann, Abstr., 1902, i, 687), may readily be obtained by the direct action of carbamide on hydrated chromic salts. When an aqueous solution containing carbamide and the greyish-blue or green hydrated chromic chloride is evaporated to a small volume on the water-bath, crystals of

carbamide and of Sell's chloride separate. The salt is not formed, however, if the solution is left to evaporate spontaneously at the ordinary temperature.

A compound, $Cr(SCN_2H_4)_3Cl_3$, is formed when a solution containing thiocarbamide and the green chromic chloride is evaporated, and may be freed from admixed thiocarbamide by treatment with 50 per cent. alcohol. It forms glistening, brownish-black, compact crystals and is insoluble in the usual organic solvents. It slowly dissolves in water, but undergoes decomposition, yielding a green solution.

J. J. S.

Two Hydrocarbons Isomeric with Campholene and Camphene. Louis Bouveault and Georges Blanc (*Compt. rend.*, 1903, **136**, 1460—1463).—*Dihydro-β-campholenetrimethylammonium iodide*, $C_8H_{15}\cdot CH_2\cdot NMe_3I$, obtained by methylation of β-aminodihydrocampholene, is crystalline and melts and decomposes at 270°; the corresponding *hydroxide* is indistinctly crystalline and soluble in water; the *platinichloride* forms sparingly soluble, orange needles.

1 : 1 : 2-*Trimethyl-3-methylene*cyclo*pentane*, $CMe_2<\begin{matrix}CHMe\cdot C{:}CH_2\\ | \\ CH_2 —— CH_2\end{matrix}$,

produced by distilling the foregoing ammonium hydroxide, is a mobile liquid which boils at 138—140° and rapidly resinifies on exposure to air; on oxidation with permanganate, it is converted into 2 : 3 : 3-trimethyl*cyclo*pentanone (Abstr., 1900, i, 202). There also results from the distillation of dihydro-β-campholenetrimethylammonium hydroxide a *base* $C_8H_{15}\cdot CH_2\cdot NMe_2$; this is a mobile liquid with a fish-like odour; it boils at 191—192° and furnishes a *platinichloride*, which crystallises in orange-red needles and melts and decomposes at 162—163°.

1 : 1 : 5-*Trimethyl-2-ethylene*-4 : 5-cyclo*pentene*,

$$CH_2{:}CH\cdot CH<\begin{matrix}CMe_2\cdot CMe\\ || \\ CH_2—CH\end{matrix},$$

similarly obtained from α-camphylamine by conversion of this into the *quaternary ammonium iodide* (prisms, melting and decomposing at 285°) and distillation of the corresponding hydroxide, is a mobile liquid with a camphene-like odour and boils at 157—158°. The *base*, $C_8H_{13}\cdot CH_2\cdot CH_2\cdot NMe_2$, produced together with the foregoing hydrocarbon, boils at 215°, has a fish-like odour, and yields a *platinichloride* which crystallises in orange-yellow needles. T. A. H.

Hydrocarbons of the *cyclo*Hexadiene Series. Carl D. Harries and Wilhelm Antoni (*Annalen*, 1903, **328**, 88—120).—A number of new dihydrobenzenes have been prepared by distilling the phosphates of the amines or diamines of the *cyclo*hexanes (compare Abstr., 1901, i, 194; and 1902, i, 361). The method is limited by the difficulty of preparing the amines; further, it is often uncertain whether a given hydrocarbon is homogeneous or a mixture of two isomerides. The determination of the position of the double linkings has often been rendered impossible by the difficulty of preparing sufficient material, and by the fact that oxidation with permanganate often entirely breaks up the compound.

$\Delta^{1:3}$-*Dihydrobenzene* ($\Delta^{1:3}$-*cyclo*hexadiene), prepared by distilling the phosphate of 1 : 3-diamino*cyclo*hexane, which is obtained by reducing dihydroresorcinoldioxime with sodium and alcohol, is a colourless liquid, becoming viscous on keeping, boils at 81·5° (corr.), and has a sp. gr. 0·8503 at 19°/19° and 0·849 at 19°/4°; it gives a red coloration with alcoholic sulphuric acid and forms a tetrabromide (m. p. 184°) with bromine, but hydrogen bromide is at the same time evolved. When oxidised with permanganate, oxalic and succinic acids are produced.

$\Delta^{1:4}$-*Dihydrobenzene* ($\Delta^{1:4}$-*cyclo*hexadiene), prepared from the phosphate of 1 : 4-diamino*cyclo*hexane, which is obtained from *p*-diketohexamethylene, is a colourless liquid boiling at 81·5° and has a sp. gr. 0·8357 at 25°/25° and 0·8333 at 25°/4°, and $n_D = 1{\cdot}46806$ at 25°; it gives with alcohol and sulphuric acid a bluish-red, and with acetic anhydride and sulphuric acid a magenta, coloration; an oily tetrabromide was obtained, from which crystals melting at 184°, separated on keeping; on oxidation, it yielded a little succinic and malonic acids.

1 : 1-*Dimethyl*-$\Delta^{2:5}$-cyclo*hexadiene* is prepared from the dioxime of dimethyldihydroresorcinol, which, on reduction with sodium and alcohol, yields 3 : 5-diamino-1 : 1-dimethyl*cyclo*hexane,

$$CMe_2<\begin{matrix}CH_2\cdot CH(NH_2)\\CH_2\cdot CH(NH_2)\end{matrix}>CH_2,$$

a clear, viscous liquid boiling at 103—105° under 9—10 mm. pressure; from the crystalline acid *phosphate* of this base, the hydrocarbon is obtained on distillation; it is a clear oil of characteristic odour, boiling at 135—137°, and has a sp. gr. 0·8433 at 18°/18° and 0·8421 at 18°/4°, and $n_D = 1{\cdot}47691$ at 18°; with concentrated sulphuric acid, it gives a deep red, and with alcohol and sulphuric acid an orange, coloration; on treatment successively with fuming nitric acid and nitric and sulphuric acids, trinitro-*m*-xylene was formed in small quantity. On oxidation with permanganate, but not with dilute nitric acid, small quantities of oxalic and succinic acids were isolated, but no dimethylmalonic acid was found. As it was expected that the 1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene, prepared by Crossley (Trans., 1902, 81, 821) also from dimethyldihydroresorcinol, would closely resemble the $\Delta^{2:5}$-isomeride, it was also prepared, but Crossley's observations were confirmed; it boils at 110—111°, has a sp. gr. 0·814 at 18°/18°, and $n_D = 1{\cdot}4563$ at 18°; with alcoholic sulphuric acid, it gives an intense dark red coloration with an indigo tint, and when treated with fuming nitric acid a small quantity of trinitro-*m*-xylene. It is suggested that this material is not homogeneous, but a mixture of di- and tetra-hydro-compounds.

Dihydro-m-*xylene* (1 : 3-*dimethyl*-$\Delta^{4:6}$-cyclo*hexadiene*?) (Harries and Atkinson, Abstr., 1902, i, 361), boils at 128—130° (corr.), has a sp. gr. 0·8203 at 18°/18°, and $n_D = 1{\cdot}4636$ at 18°; with sulphuric acid, it gives an orange, with sulphuric acid and alcohol a yellow, and with sulphuric acid and acetic anhydride a red, coloration. By the action of fuming nitric acid, trinitro-*m*-xylene is obtained, but not in such good yield as from the dihydro-*m*-xylene prepared from methylheptenone (Wallach).

Cantharene (dihydro-*o*-xylene), prepared from calcium cantharate (Piccard, *Ber.*, 1878, 11, 2122) and boiling at 130—140°, is shown by a determination of the refractive index ($n_D = 1{\cdot}49118$) to be a mixture

of dihydro-*o*-xylene and *o*-xylene; it gives an orange coloration both with sulphuric acid and with sulphuric acid and alcohol, but with acetic anhydride and sulphuric acid a reddish-brown coloration.

Dihydro-m-*cymene*, $\begin{matrix}\text{CMe}\cdot\text{CH}_2\cdot\text{CHPr}^\beta \\ \text{||} \qquad\qquad\quad | \\ \text{CH—CH:CH}\end{matrix}$ or $\begin{matrix}\text{CMe:CH}\cdot\text{CHPr} \\ | \qquad\qquad | \\ \text{CH:CH}\cdot\text{CH}_2\end{matrix}$, is prepared from 1-methyl-3-*iso*propylhexenone, which is first converted into the oxamino-oxime by means of hydroxylamine, and then reduced, whereby 1 : 3-*diamino*-m-*menthane* is formed; the latter is a colourless liquid boiling at 115—117° under 13 mm. pressure and yields the cymene when the phosphate is distilled; the hydrocarbon boils at 172—174° (corr.) and has a sp. gr. 0·8423 at 18·5°/18·5° and 0·8411 at 18·5°/4°, and $n_D = 1{\cdot}47936$ at 18·5°. With sulphuric acid, it gives a red, with sulphuric acid and alcohol an orange, and with acetic anhydride and sulphuric acid a bluish-violet, coloration. When oxidised by permanganate in aqueous solution, oxalic and succinic acids are formed, but in acetone solution a 1 : 4-diketone is produced; the hydrocarbon is not attacked by the chromic acid mixture. K. J. P. O.

A New Synthesis of Hydrocarbons. ALFRED WERNER and F. ZILKENS (*Ber.*, 1903, 36, 2116—2118).—Phenyl magnesium bromide in ethereal solution reacts very readily with methyl sulphate at the ordinary temperature, 32 per cent. being converted into toluene, whilst a small quantity of diphenyl is also formed. Better results are obtained from the interaction of *p*-tolylmagnesium bromide and methyl sulphate when 75 per cent. is converted into *p*-xylene. It is essential that the ether is highly purified. E. F. A.

Transformation of Diphenyliodonium Iodide and Chloride and its Velocity. ERNST H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 646—650).—The transformation of diphenyliodonium iodide into iodobenzene ($Ph_2I{\cdot}I = 2PhI$) is an irreversible reaction. The change takes place under the influence of light at temperatures considerably below the melting point. In the dark at 90°, one per cent. is changed in three hours, but the rate is very greatly influenced by the presence of small quantities of impurity. The chloride is more stable than the iodide.

The velocity of decomposition of the chloride in aqueous solution at 98—99° was determined. The results calculated by the van't Hoff formula show that the reaction is a bimolecular one. The addition of hydrochloric acid greatly retards the decomposition, whereas the addition of diphenyliodonium hydroxide greatly increases it. It is probable that the reaction does not take place between the ions but between two molecules. A trace of iodine retards the transformation. J. McC.

Electrolytic Reduction of *p*-Nitrotoluene Dissolved in Hydrochloric Acid in Presence of Formaldehyde. EMIL GOECKE (*Zeit. Elektrochem.*, 1903, 9, 470—473).—The author has reinvestigated the base obtained by Löb (Abstr., 1899, i, 123) by the electrolytic reduction of *p*-nitrotoluene in presence of formaldehyde and has com-

pared it with the substances obtained by Troeger (Abstr., 1888, 286) by the action of nascent formaldehyde on *p*-toluidine and by Eberhardt and Welter (Abstr., 1894, i, 451) and Eibner (Abstr., 1899, i, 41) by the action of formaldehyde on an alcoholic solution of *p*-toluidine. The three products are identical, and when pure melt at 136°. Analyses show the substance to have the formula $(C_8H_9N)_n$, but attempts to determine the value of n by the boiling point method, using ether as solvent, were unsucsessful. The author considers, however, that $n = 3$ is the most probable value and that the substance is to be regarded as a derivative of trimethylenetriamine. T. E.

Nitration of the Low Boiling Fractions of Galician Petroleum. Romain Zaloziecki (*Bull. Acad. Sci. Cracow*, 1903, 4, 228—229. Compare Abstr., 1902, i, 197).—Petroleum from Kryg was fractionated and the portion boiling at 40—101° was further subdivided into three fractions boiling at 40—65°, 65—85°, and 85—101° respectively, each of which was then nitrated and the products separated by fractional crystallisation from alcohol and benzene. From the fraction boiling at 40—65°, *m*-dinitrobenzene, trinitro*iso*hexane, and a mixture of *m*-dinitrobenzene and dinitrotoluene were obtained; the fraction boiling at 65—85° yielded 2 : 4-dinitrotoluene, along with much *m*-dinitrobenzene and a dinitro-compound melting at 66—67°, whilst the third fraction yielded mainly 2 : 4-dinitrotoluene, together with 2 : 5-dinitrotoluene and a dinitroxylene melting at 39—40°. From a fraction melting at 29·5—31·5°, 1 : 2-dimethyl-3 : 4-dinitrobenzene was isolated. A. McK.

Nitroaminohydroxytoluene-ω-sulphonic Acid. Kalle & Co. (D.R.-P. 141783).—*o*-Chlorobenzyl chloride reacts with sulphites to form *o*-chlorobenzylsulphonic acid [*o* chlorotoluene-ω-sulphonic acid], the sodium salt of which crystallises from alcohol in leaflets. It reacts with 2 mols. of nitric acid to form *chlorodinitrotoluene-ω-sulphonic acid*, the *calcium* salt of which crystallises from water or alcohol in colourless needles. On heating the acid with ammonia at 135—140°, the chlorine atom and one nitro-group, probably that occupying the *o*-position to the chlorine atom, are replaced by the amino-group. The resulting *nitroaminohydroxytoluene-ω-sulphonic acid* is difficult to prepare in a pure state, but forms crystalline yellow salts and a readily soluble *diazonium* compound. C. H. D.

Reduction of ω-Nitrostyrolene (β-Nitrostyrene). Louis Bouveault and André Wahl (*Bull. Soc. chim.*, 1903, [iii], 29, 519—521. Compare Priebs, Abstr., 1884, 313, and this vol., i, 596).—When β-nitrostyrene, dissolved in ether, is reduced by zinc and acetic acid, phenylacetaldoxime is formed. The reduction may also be brought about by aluminium amalgam, but the yield of the oxime obtained is less.

T. A. H.

Preparation and Reduction of Homologues of Nitrostyrolene (β-Nitrostyrene). Louis Bouveault and André Wahl (*Bull. Soc. chim.*, 1903, [iii], 29, 521—528. Compare Abstr., 1902, i,

682; Thiele, Abstr., 1899, i, 584; Thiele and Haeckel, this vol., i, 160, and preceding abstract).—Most of this work has already been published (*loc. cit.*). When piperonylidenenitromethane is reduced there is formed in addition to homopiperonylaldoxime a small quantity of a *substance* which separates from boiling acetic acid in crystalline grains and melts at 155°. β-*o*-Dinitrostyrene, when reduced, is converted into an unstable oil. T. A. H.

Homologues of Propenyl- and Butenyl-benzene. FRANZ KUNCKELL (*Ber.*, 1903, 36, 2235—2237. Compare this vol., i, 331). —*p*-Methylallylbenzene, prepared by the action of sodium on 1-methyl-4-α-chloro-β-bromoallylbenzene, boils at 83—85° under 10 mm. pressure and has the sp. gr. 0·9057 at 13° (compare Klages, Abstr., 1902, i, 612). 1 : 3-*Dimethyl*-4-*allylbenzene*, prepared from 1 : 3-dimethyl-4-α-chloro-β-bromoallylbenzene, boils at 85—88° under 10 mm. pressure and has the sp. gr. 0·903 at 13°; its *dibromide* boils at 151—153° under 9 mm. pressure. 1 : 2-*Dimethyl*-4-*allylbenzene* boils at 165—168° under 16 mm. pressure and has the sp. gr. 0·9151 at 18°. p-*Ethylallylbenzene* boils at 105—107° under 17 mm. pressure and has the sp. gr. 0·9072 at 18°. p-iso*Propylallylbenzene* boils at 121—125° under 19 mm. pressure and has the sp. gr. 0·9308 at 22°. 1-*Methyl*-4-iso*propyl*-3 *allylbenzene* boils at 128—131° under 32 mm. pressure and has the sp. gr. 0·8899 at 18°. 1-*Methyl*-4-α-*butenylbenzene* boils at 210—212° and has the sp. gr. 0·8893 at 20°. 1 : 3-*Dimethyl*-4-α-*butenylbenzene* boils at 109—111° under 16 mm. pressure and has the sp. gr. 0·8967 at 18°. A. McK.

The Friedel and Crafts' Reaction. III. JACOB BOESEKEN (*Rec. trav. chim.*, 1903, 22, 301—314. Compare Abstr., 1900, i, 349, and 1901, i, 474).—Chloroform dissolves small quantities of aluminium chloride, and on evaporating the solution a hygroscopic, gummy mass is obtained, which approximates in composition to the *compound* $CHCl_3,AlCl_3$, and is decomposed by benzene, giving diphenylmethane and triphenylmethane. When chloroform (45 grams) is gradually added to an excess of benzene containing aluminium chloride, a mixture of diphenylmethane (6 grams), triphenylmethane (11·6 grams), and triphenylchloromethane, CPh_3Cl (24·1 grams) is formed. That the last two substances are not produced by a preliminary decomposition of the chloroform, according to the equation $2CHCl_3 = CCl_4 + CH_2Cl_2$, is shown by the fact that pure chloroform can be distilled from aluminium chloride without undergoing change. It is more probable that the action of the chloroform takes place in the stages: I. $CHCl_3,AlCl_3 + C_6H_6 \rightarrow CHPhCl_2,AlCl_3$; II. $CHPhCl_2,AlCl_3 + C_6H_6 \rightarrow CHPh_2Cl,AlCl_3$; III. $CHPh_2Cl,AlCl_3 + C_6H_6 \rightarrow CHPh_3$, and that the diphenylchloromethane decomposes thus: $2CHPh_2Cl \rightarrow CH_2Ph_2 + CPh_2Cl_2$, giving diphenylmethane and dichlorodiphenylmethane, the latter interacting with benzene to form triphenylchloromethane. That this explanation is correct appears probable from the fact that diphenylchloromethane (25 grams) combines with benzene, giving triphenylchloromethane (10·7 grams) and diphenylmethane (7·8 grams) as principal products, with only a trace (10·7 grams) of triphenyl-

methane; but attempts to decompose diphenylchloromethane by aluminium chloride according to the equation $2CHPh_2Cl = CH_2Ph_2 + CPh_2Cl_2$ give only resinous products.

When benzylidene dichloride (30 grams) is condensed with benzene in presence of aluminium chloride, triphenylchloromethane (11·0 grams), triphenylmethane (6·1 grams) and diphenylmethane (3·0 grams) are formed; the proportions of the products are nearly the same as are obtained with chloroform, and it appears probable that the direct decomposition $2CHPhCl_2 = CH_2PhCl + CPhCl_3$ does not occur.

W. A. D.

Action of Zinc on Triphenylchloromethane. II. JAMES F. NORRIS (*Amer. Chem. J.*, 1903, 29, 609—616. Compare Norris and Culver, this vol., i, 333; Gomberg, this vol., i, 472).—Controversial.

A. McK.

[Attempts to Prepare Aniline and Carbamide Magnesium Phosphates.] CH. PORCHER and M. BRISAC (*Bull. Soc. chim.*, 1903, [iii], 29, 593—594).—All attempts to prepare aniline and carbamide magnesium phosphates failed.

N. H. J. M.

Preparation of Aromatic Nitroamines from Phthalimides. RUDOLF LESSER (D.R.-P. 141893).—In the nitration of aromatic amines, the group employed to protect the amino-group (acetyl, benzoyl, &c.) is either completely lost in the subsequent hydrolysis, or, as in the case of benzylideneaniline, recovered as benzaldehyde with considerable loss. This is avoided by the employment of phthalimides. Thus phthalanil yields *p*-nitrophthalanil on nitration, which, when heated with aniline at 170—180° under pressure, forms *p*-nitroaniline, the phthalanil being recovered for repeated use. Similarly, dinitrophthalanil and aniline yield 2 : 4-dinitroaniline; *p*-tolylphthalimide and *p*-toluidine form 2-nitro-4-toluidine, and phthalyl-*o*-iminobenzoic acid and aniline yield phthalanil and a mixture of 5- and 4-nitro-2-aminobenzoic acids. The nitrated phthalimides may also be heated with bases other than those employed in the preparation of the original condensation product.

C. H. D.

Thiouram Sulphides and the Action of Cyanides on Disulphides. JULIUS VON BRAUN and F. STECHELE (*Ber.*, 1903, 36, 2275—2285).—When disubstituted dithiocarbamates are acted on in alcoholic solution by cyanogen bromide or iodide (1 mol.), tetra-alkylthiouram disulphides are formed. When the cyanogen haloid is taken in the proportion of ½ mol., intensely yellow substances of the composition $S_3C_2(NR_2)_2$ are produced, which can be synthesised by the action of dithiocarbamates on thiocarbamine chlorides, thus:

$$NR_2{\cdot}CS{\cdot}SH,HNR_2 + Cl{\cdot}CS{\cdot}NR_2 = S(CS{\cdot}NR_2)_2 + HNR_2,HCl.$$

The colourless thiouram disulphides are converted by potassium cyanide into the coloured monothiouram sulphides, thus: $S_2(CS{\cdot}NR_2)_2 + KCN = S(CSNR_2)_2 + KCNS$. When dimethyl- or diethyl-thiouram disulphide is gently warmed with potassium cyanide, phenylthiocarbimide and hydrogen sulphide are evolved, whilst thiocyanic acid can be detected in the solution. Tetramethylthiouram

disulphide, when gently warmed with an aqueous alcoholic solution of potassium cyanide, gives an almost theoretical yield of the *tetramethylthiouram monosulphide*, $S(CS\cdot NMe_2)_2$, which may likewise be prepared by the action of cyanogen bromide or iodide on dimethylamine dimethyldithiocarbamate; it melts at 104°, whilst tetramethylthiouram disulphide melts at 146°. The same monosulphide is also formed by interaction of dimethylthiocarbamine chloride and dimethylamine dimethyldithiocarbamate. It is very stable towards acids and is more easily attacked by alkalis with formation of dimethylamine. It is readily attacked by primary amines; with benzylamine, for example, a vigorous evolution of hydrogen sulphide takes place, dibenzylthiocarbamide (m. p. 146°) being formed.

Dipiperidylthiouram monosulphide, $S(CS\cdot C_5NH_{10})_2$, prepared by boiling dipiperidylthiouram disulphide with potassium cyanide, melts at 120°.

Diphenyldimethylthiouram monosulphide, $S(CS\cdot NMePh)_2$, melts at 150—151°, whilst the corresponding *diethyl* compound melts at 115°. The former, on being boiled with aniline, forms diphenylthiocarbamide, melting at 151°.

Dimethylamine dimethyldithiocarbamate and phenylethylthiocarbamine chloride give the as-*phenyldimethylethylthiouram sulphide*, $NMe_2\cdot CS\cdot S\cdot CS\cdot NEtPh$, melting at 95°.

When phenylmethyl- or phenylethyl-thiocarbamine chloride acts on methylamine methyldithiocarbamate and the product is treated with water, yellow, viscid oils are formed, which, under the influence of iodine and alcoholic potash, yield phenylthiocarbimide and phenylmethyl- or phenylethyl-thiouram disulphide, melting respectively at 150° and 186°. From phenylmethyl*iso*thiouram disulphide, *iso*thiouram disulphide, melting at 84—85°, was isolated. A. McK.

Thiouram Disulphides and *iso*Thiouram Disulphides. II. Julius von Braun (*Ber.*, 1903, 36, 2259—2274. Compare Abstr., 1902, i, 271).—*iso*Thiouram disulphides very readily decompose into thiocarbimides and disulphides, thus: $S_2[C(:NR)SR']_2 = 2SC:NR + S_2R'_2$. This is the first example of the decomposition of a complicated disulphide compound which takes place without separation of sulphur. The salt of an alkylated thiouram disulphide behaves towards halogen compounds like a metallic sulphide such as sodium disulphide.

The preparation of aliphatic and hydroaromatic *iso*thiouram disulphides is difficult. [With K. Rumpf.] Aromatic *iso*thiouram disulphides, on the other hand, are easily prepared from dithiourethanes, sodium ethoxide, and iodine, aromatic thiocarbimides and disulphides being simultaneously formed. Aromatic *iso*thiouram disulphides do not form salts with acids, nor do they unite with alkyl haloids. Strong sulphuric acid causes evolution of mercaptan from them, and reducing agents convert them into dithiourethanes.

N-*Diphenyl*-S *dimethyl*iso*thiouram disulphide*, $S_2[C(:NPh)\cdot SMe]_2$, forms snow-white crystals melting at 123°. When heated at 100—130°, no separation of sulphur takes place, but phenylthiocarbimide and methyl disulphide are formed. When reduced by hydrogen sulphide, *phenylmethyldithiourethane* melting at 93·5° is formed.

N-*Diphenyl*-S-*diallyl*iso*thiouram disulphide* melts at 74—75° and is more readily decomposable than the methyl compound, complete decomposition taking place at 90—95°. The thiocarbimide and allyl disulphide produced were identified.

N-*Diphenyl*-S-*dibenzyl*iso*thiouram disulphide* melts at 121° and decomposes at 105° to give benzyl disulphide (m. p. 70°).

In the preparation of aliphatic *iso*thiouram disulphides, thiocarbimides and alkyl disulphides were, as a rule, formed in much larger quantities when dithiourethanes were used as the source instead of thiouram disulphides. The formation of aliphatic *iso*thiouram disulphides (*loc. cit.*) is accompanied by that of the corresponding thiocarbimides and alkyl disulphides. Di*iso*propylthiouram disulphide and methyl iodide or dimethylthiouram disulphide and *iso*propyl iodide give a small yield of *iso*disulphides.

By the action of methylene iodide on sodium dimethylthiouram disulphide, the *iso*disulphide, $\begin{matrix} S\cdot C(:NMe)\cdot S \\ S\cdot C(:NMe)\cdot S \end{matrix}>CH_2$, melting at 118°, is formed (mixed, however, with a trace of an impurity, probably methylene disulphide); this compound, in contradistinction to the aliphatic *iso*thiouram disulphides, is remarkably stable, not being attacked by acids or alkalis. *o*- and *p*-Xylylene bromides yield, with dialkylthiouram disulphides, the corresponding nitrogen-free disulphides.

Disulphides of acids are prepared by condensing thiouram disulphides with acid chlorides. Benzoyl chloride and dimethyl- or diethylthiouram disulphide give *benzoyl disulphide*, which melts at 133°.

Cinnamoyl disulphide, prepared in analogous manner, melts at 139°, and, like benzoyl disulphide, when heated above its melting point, assumes a red colour.

Tetraphenylcarbamine disulphide, $S_2(CO\cdot NPh_2)_2$, prepared by the action of diphenylcarbamine chloride on dimethylthiouram disulphide, forms white crystals melting at 195—196°. By the action of dibenzyl- and dipropylcarbamine chlorides respectively on thiouram disulphides, oils were formed instead of the customary solids. Thiocarbamine chlorides act on dialkylated thiouram disulphides to form tetra-alkylated thiouram disulphides. The disulphides, $S_2(CS\cdot NMePh)_2$ and $S_2(CS\cdot NEtPh)_2$, when crystallised from alcohol melt at 198° and 170° respectively.
A. McK.

Cyclic Ketones from Chloroform and Phenols. III. Karl Auwers and G. Keil (*Ber.*, 1903, 36, 1861—1877. Compare Abstr., 1902, i, 218; this vol., i, 100).—1-*Hydroxy*-1 : 4-*dimethyl*-4-*dichloromethyldihydrobenzene*, $OH\cdot CMe<\begin{matrix} CH:CH \\ CH:CH \end{matrix}>CMe\cdot CHCl_2$, obtained by the action of methyl iodide and magnesium on the dichloro-ketone, $CO<\begin{matrix} CH:CH \\ CH:CH \end{matrix}>CMe\cdot CHCl_2$, prepared from *p*-cresol and chloroform, crystallises from light petroleum in concentrically grouped aggregates of slender needles, melts at 96°, and is shown to be an alcohol by the cryoscopic values obtained with its solution in benzene. It is unstable at the ordinary temperature, its melting point falling 10° in a day,

whilst after several days the crystals have changed to a thick, brown oil. All attempts to prepare alkyl or acidyl derivatives were fruitless, and even phenylcarbimide failed to give a phenylurethane. In all cases, a product, $C_9H_{10}Cl_2$, is formed by the loss of $1H_2O$ from the original substance, which boils at 115·8—116·8° under 12·5 mm., at 120·2—122·7° under 18 mm., and at 236—238° under the ordinary pressure; it has a sp. gr. 1·1709 at 17°/17°, n_D 1·53804 at 17°, and a mol. refraction showing the presence of three double linkings. Apparently this substance is a *ω-dichloro-*p*-methylethylbenzene*, $CHCl_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_3$ or $C_6H_4Me \cdot CH_2 \cdot CHCl_2$, but attempts to convert it into a corresponding aldehyde or ketone by heating with boiling aqueous baryta or silver acetate leave it unchanged; water at 170—180°, however, converts it into a *hydrocarbon*, $C_{18}H_{16}$, which crystallises from light petroleum in nacreous leaflets, melts at 140—141°, and is formed by loss of 4HCl from 2 mols. of the chloride. By sodium, in boiling absolute alcoholic solution, it is reduced to *p*-methylethylbenzene, which boils at 161·6—162·5° under 76 mm. pressure, and forms a dinitro-derivative melting at 51—52° and a trinitro-compound melting at 94° (Jannasch and Dieckmann, Abstr., 1875, 1189, give 51—52° and 92° respectively).

The dichloro-*p*-methylethylbenzene is probably formed by the initial production of a methylene compound, thus:

$$OH \cdot CMe<^{CH:CH}_{CH:CH}>CMe \cdot CHCl_2 \longrightarrow CH_2:C<^{CH:CH}_{CH:CH}>CMe \cdot CHCl_2,$$

which then undergoes isomeric change; that the stages are not

$$OH \cdot CMe<^{CH:CH}_{CH:CH}>CMe \cdot CHCl_2 \longrightarrow \cdot CMe<^{CH:CH}_{CH:CH}>CMe \cdot CCl_2 \cdot$$
$$\longrightarrow CMe \lessdot^{CH:CH}_{CH \cdot CH} \gtrdot CCl_2Me$$

is shown by the fact that the *p*-methylacetophenone chloride, $C_6H_4Me \cdot CMeCl_2$, which is prepared by the action of phosphorus pentachloride on *p*-methylacetophenone, differs from the chloro-compound described above in decomposing when distilled under diminished pressure, giving *α-chloro-*p*-methylstyrene*, $C_6H_4Me \cdot CCl:CH_2$, which boils at 96—97·5° under 13 mm. pressure. Moreover, the chloride of *p*-methylacetophenone, after distillation, when heated with water at 170—180°, does not give a hydrocarbon, but regenerates the ketone.

p-*Methylbenzylidene chloride*, $C_6H_4Me \cdot CHCl_2$, prepared from phosphorus pentachloride and *p*-tolualdehyde, crystallises from alcohol in long, flattened needles, melts at 48—49°, and is easily reconverted into the aldehyde by heating it with water at 170—180°. W. A. D.

Formation of Derivatives of Diphenylmethane from *pseudo*-Phenols and Allied Compounds. KARL AUWERS (*Ber.*, 1903, 36, 1878—1893).—The substances formed by the action of alkalis on the *pseudo*-phenols are not, as hitherto supposed, stilbene derivatives, but are derived from dihydroxydiphenylmethane; their formation is probably due to the intermediate productions of a methylenequinone, $2\,O:C_6H_4:CH_2 + H_2O = OH \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot OH + CH_2O$.

3 : 5-Dibromo-4-hydroxybenzyl bromide, which is best prepared by

brominating 3 : 5-dibromo-*p*-cresol at 138—140°, combines with pyridine dissolved in benzene to form the additive *compound*,

$$OH\cdot C_6H_2Br_2\cdot CH_2\cdot C_5NH_5Br;$$

this crystallises from glacial acetic acid in thick, colourless prisms, melts and decomposes at 186—190°, and is converted by aqueous sodium carbonate containing a little sodium hydroxide principally into 3 : 5 : 3′ : 5′-tetrabromo-4 : 4′-dihydroxydiphenylmethane, which crystallises from glacial acetic acid in long, white needles with $2C_2H_4O_2$, melts at 226—227°, and is identical with Staedel's compound prepared from *p*-dihydroxydiphenylmethane (*Annalen*, 1894, **283**, 163), as is shown by a comparison of their dimethyl ethers and diacetates, and their giving, on reduction with sodium amalgam, 4 : 4′-dihydroxydiphenylmethane.

For purposes of comparison, 3 : 5 : 3′ : 5′-*tetrabromo*-4 : 4′-*dimethoxystilbene dibromide*, $C_2H_2Br_2(C_6H_2Br_2\cdot OMe)_2$, was prepared by brominating 4 : 4′-dimethoxystilbene; it crystallises in thin leaflets, melts and decomposes at 228—230°, and when heated with copper powder in xylene loses 2HBr, giving 3 : 5 : 3′ : 5′-*tetrabromo*-4 : 4′-*dimethoxystilbene*, $C_2H_2(C_6H_2Br_2\cdot OMe)_2$, which crystallises in transparent needles and melts at 279—280°.

The additive *compound*, formed by pyridine with bromo-*p*-hydroxy-ψ-cumylbromide [$Me_2 : OH : Br : CH_2Br = 1 : 4 : 2 : 3 : 5$] (Auwers and Ercklentz, Abstr., 1899, i, 35), crystallises in flat, lustrous needles, melts and decomposes at 221—223°, and is converted by alkali hydroxides into 3 : 3′-*dibromo*-4 : 4′-*dihydroxy*-2 : 5 : 2′ : 5′-*tetramethyldiphenylmethane*, which crystallises from glacial acetic acid in thick, lustrous, yellowish prisms and melts at 152—153°. The *diacetyl* derivative forms small, nodular aggregates of needles and melts at 178—179°.

4 : 4′-*Dihydroxy*-2 : 5 : 2′ : 5′-*tetramethyldiphenylmethane*, obtained by reducing the bromo-compound with sodium amalgam, crystallises from dilute acetic acid or alcohol in small, thick prisms, melts at 181—182°, and gives a *diacetate*, which crystallises in silky needles melting at 154—155°.

4 : 4′-*Dihydroxy*-2 : 5 : 2′ : 5′-*tetramethyldiphenyltrichloroethane*,

$$CCl_3\cdot CH[C_6H_2Me_3(OH)]_2,$$

obtained by condensing *p*-xylenol with chloral hydrate in presence of concentrated sulphuric acid, crystallises from dilute alcohol in short, thick, colourless prisms and melts at 175—176°; on reduction with zinc dust in alcoholic solution, it gives 4 : 4′-*dihydroxy*-2 : 5 : 2′ : 5′-*tetramethylstilbene*, which crystallises from nitrobenzene in brownish-yellow, lustrous needles, melts at 320—330°, and yields a *diacetyl* derivative melting at 154—155°. W. A. D.

Preparation of *o*-Chlorophenol. Maurice Hazard-Flamand (D.R.-P. 141751).—Phenol-*p*-sulphonic acid is chlorinated at about 50°, and the resulting *o*-chlorophenol-*p*-sulphonic acid decomposed into *o*-chlorophenol and sulphur trioxide, either by heating the sodium salt, containing a little free acid, at 180—200°, or by heating the acid with water under pressure at the same temperature. A pure product is obtained. C. H. D.

Constitution of the Nitrophenols and Nitroanilines. Robert Hirsch (*Ber.*, 1903, **36**, 1898—1899).—When dilute aqueous solutions of the sodium salts of the three nitrophenols are heated, those of the *o*- and *p*-compounds become much darker in colour, whilst the colour of the solution of the *m*-compound remains unchanged. That the change of colour is not due to electrolytic dissociation is shown by the fact that, on cooling, the original colour is restored only very slowly, not being quite the same after several days. The author considers that in solution salts of *o*- and *p*-nitrophenol can exist in two forms, a normal and a quinonoid.

When a drop of alcoholic potassium hydroxide is added to an alcoholic solution of *o*-nitroaniline, the colour changes from orange to blood-red; with *p*-nitroaniline, the change is from yellow to yellowish-brown, but with *m*-nitroaniline there is no alteration. That the change of colour is due to the formation of a salt is considered most probable, since a cold saturated solution of the nitroaniline, which is made to dissolve 1 per cent. more of solid by warming, fails to deposit this as crystals on cooling after adding a few drops of alkali.

W. A. D.

Simultaneous Formation of Isomeric Substitution Derivatives of Benzene. VII. Nitration of the Nitroanisoles. Arnold F. Holleman (*Rec. trav. chim.*, 1903, **22**, 263—280).—On gradually adding *o*-nitroanisole to a mixture of 1 vol. of nitric acid of sp. gr. 1·4 and 6 vols. of sulphuric acid of sp. gr. 1·52 at 0°, 86·2 per cent. of 2 : 4-dinitroanisole, and 13·8 per cent. of 2 : 6-dinitroanisole are obtained; *p*-nitroanisole under similar conditions gives 2 : 4-dinitroanisole as the sole product; but *m*-nitroanisole gives a mixture of 51·2 per cent. of 2 : 3-dinitroanisole, 40·6 per cent. of 3 : 6-dinitroanisole and 8·2 per cent. of the 3 : 4-dinitro-compound. The composition of the products of nitration was established by the method of solidifying points (compare Abstr., 1900, i, 638) and of sp. gr. (Abstr., 1900, i, 387).

Whereas the nitration of *o*- and *p*-nitroanisoles is normal, that of the meta-compound is unusual; it is obvious that the methoxyl radicle here exercises a predominant influence. The formation of 3 : 6-dinitroanisole would not have been anticipated. W. A. D.

Nitration of *s*-Dinitroanisole. Jan J. Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, **5**, 650—652).—If *s*-dinitroanisole is nitrated on the water-bath with a mixture of nitric acid of sp. gr. 1·44 and sulphuric acid, *trinitroanisole*, which melts at 104°, is formed. The introduced nitro-group is easily replaceable by the hydroxy-, methoxy-, amino-, or methylamino-group, and it has been proved that the trinitroanisole formed has the constitution

$$OMe\cdot C_6H_2(NO_2)_3 = 1:2:3:5,$$

the third nitro-group having entered the *ortho* position with respect to the methoxy-group.

When treated with a solution of sodium methoxide in methyl alcohol, the nitro-(2)-group is replaced by a methoxy-group and *dinitrocatechol dimethyl ether* is formed, which melts at 101°. With alcoholic

ammonia, it yields *dinitroanisidine*, $OMe\cdot C_6H_2(NH_2)(NO_2)_2 = 1:2:3:5$, which melts at 174°; with aniline and ethylamine, derivatives are formed which melt at 155° and 132° respectively.

Trinitroanisole, when nitrated with nitric acid of sp. gr. 1·52 and sulphuric acid, gives *tetranitroanisole*, which melts at 154° and on treatment with 2 mols. of sodium methoxide gives crystals melting at 165°, which assume a purple-brown colour when exposed to light. This substance is identical with that formed by the action of sodium methoxide on *s*-tribromodinitrobenzene (Jackson and Warren, Abstr., 1891, 1024), and is therefore *dinitrophloroglucinol trimethyl ether*, $C_6H(OMe)_3(NO_2)_2 = 1:3:5:2:6$, and the tetranitroanisole has the constitution $C_6H(OMe)(NO_2)_4 = 1:2:3:5:6$.

When *s*-tribromodinitrobenzene is treated with 6 mols. of methylamine in alcoholic solution, the three bromine atoms are replaced by methylamino-groups and the compound $C_6H(NO_2)_2(NHMe)_3 = 1:3:5:2:6$ is formed as orange-red needles which melt at 220°. When dissolved in nitric acid of sp. gr. 1·52 and then diluted with water, a white, crystalline powder of *s-trinitrophenyltrimethyltrinitramine*,

$$C_6[N(NO_2)Me]_3(NO_2)_3 = 1:3:5:2:4:6,$$

is formed, which separates from acetic acid in white needles and explodes at 200—203°. J. McC.

Behaviour of *p*-Alkylated Phenols towards Caro's Reagent. EUGEN BAMBERGER (*Ber.*, 1903, 36, 2028—2041).—*p*-Tolu-ψ-quinol, $O{:}C_6H_4Me\cdot OH$, prepared by the action of Caro's reagent on *p*-cresol, is identical with that obtained by the action of dilute sulphuric acid on *p*-tolylhydroxylamine. *as-m*-Xylenol is similarly converted into xylo-ψ-quinol hydrate. Mesitol gave mesityl-ψ-quinol, but also *4-hydroxy-3:5-dimethylbenzyl alcohol*, $HO\cdot C_6H_2Me_2\cdot CH_2\cdot OH$, which crystallises from benzene or water in white, silky needles, melts at 104·5—105°, and is volatile in steam superheated to 110—120°; it is oxidised by ferric chloride to 1:3-dimethyl-2:5-quinone, and was also prepared from 2:6-dimethylphenol (this melts at 44—46°, not at 49°). ψ-Cumenol is oxidised to 3:4:6-trimethyl-ψ-quinol and di-ψ-cumenol.

2:6-Dimethylphenylhydroxylamine is converted by methyl alcohol and sulphuric acid into *2:6-dimethyl-1:4-anisidine*,

$$NH_2\cdot C_6H_2Me_2\cdot OMe,$$

which crystallises from light petroleum in white, pearly flakes, melts at 42·5—43°, and is oxidised by ferric chloride to 1:3-dimethyl-2:5-quinone. *4-Methoxy-2:6-dimethylphenol*, prepared by the action of nitrous acid on the amine, crystallises from light petroleum in white, silky needles, melts at 77—77·5°, is volatile with steam, and is oxidised by ferric chloride to *m*-xyloquinone. T. M. L.

Nitration of Guaiacol Acetate. FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1903, 36, 2257—2258).—Guaiacol *p*-toluenesulphonate, when nitrated at the temperature of the water-bath, yields a mononitro-derivative melting at 145° and giving on hydrolysis a mononitroguaiacol melting at 105° (compare Meldola, Proc., 1896, 12, 125). When the latter compound, which is probably 4-nitro-1-hydroxy-2-methoxy-

benzene, is acetylated, the product crystallises in white needles melting at 101°. Barbier found that nitroguaiacol acetate, prepared by nitrating guaiacol acetate, melted at 135—136°. The authors have repeated Barbier's experiments and find that, when guaiacol acetate is nitrated in the cold, the acetyl grouping is split off and dinitroguaiacol, melting at 122°, is formed. When the nitration is conducted at 100°, the acetyl group is not split off, but mononitroguaiacol acetate, melting at 101°, is produced. This, on hydrolysis, yielded nitroguaiacol, melting at 105° and identical with the substance obtained from guaiacol *p*-toluenesulphonate. A. McK.

Trialkyl Ethers of Hydroxyquinol. OTTO KULKA (*Chem. Zeit.*, 1903, **27**, 407—408).—When hydroxyquinol triacetate is added to alcoholic sodium methoxide or ethoxide, the alkyl acetate is formed and the sodium derivative of hydroxyquinol remains in solution; on adding methyl or ethyl iodide and boiling the liquid for 24 hours, the trialkyl ether is formed in 70 per cent. yield. The sodium derivative can also be methylated by using methyl sulphate. 1 : 2 : 4-*Trimethoxybenzene* is colourless and boils at 247°. W. A. D.

Cholesterol. I. HUGO SCHRÖTTER (*Monatsh.*, 1903, **24**, 220—228).—When cholesterol was subjected to exhaustive bromination and the products fractionated, two products were obtained—a *nonobromide* of dehydrocholesterol, $C_{23}H_{27}OBr_9$, melting at about 145°, and a *hexabromide*, $C_{27}H_{26}OBr_6$, melting at about 112°. Either of these gave rise on reduction to the formation of a dark brown, amorphous substance, which could not be purified, mixed with small quantities of a partially crystalline bromide melting at 62—64°, probably the *dibromide* of dehydrocholesterol. Strong nitric acid converts this into an acid of the composition $C_{27}H_{21}O_{12}N_3Br_2$, which decomposes on heating at about 198°. These results point to the splitting off of 12 hydrogen atoms from cholesterol, $C_{27}H_{44}O$, under the action of bromine.

E. F. A.

Cholesterol. V. JULIUS MAUTHNER and WILHELM SUIDA (*Monatsh.*, 1903, **24**, 175—195. Compare Abstr., 1896, i, 425).—By the oxidation of cholesterol, three closely related acids are formed which can be separated by the different solubility of their calcium salts in hot aqueous alcoholic solutions. With nitric acid, the chief product is an acid $C_{12}H_{16}O_8$. Permanganate at low temperatures gives rise to an acid $C_{13}H_{18}O_8$, whilst at higher temperatures the product is an acid $C_{14}H_{20}O_9$; but probably in each case small quantities of all three acids are formed as well as various other acid oxidation products. Further, the acid $C_{12}H_{16}O_8$ loses water to form an anhydride, $C_{24}H_{30}O_{15}$, which is also found among the oxidation products obtained with permanganate. Probably also this acid loses carbon dioxide, as an acid $C_{11}H_{16}O_6$ was frequently observed. These acids are all amorphous, badly defined compounds; they have been characterised by repeated analysis of their calcium and copper salts. E. F. A.

The Glycol obtained from *iso*Butaldehyde and Cuminaldehyde, and its Behaviour with Dilute Sulphuric Acid. FRIEDRICH SCHUBERT (*Monatsh.*, 1903, 24, 251—260. Compare Reik, Abstr., 1898, i, 245, and Lieben, Abstr., 1902, i, 336).—The *glycol*, $C_{14}H_{22}O_2$, obtained by the action of potassium hydroxide on *iso*butaldehyde and cuminaldehyde, forms a crystalline mass, melts at 58°, and boils at 181·5° under 8·5 mm., at 210° under 22 mm. pressure. The *diacetyl* derivative is an oil which boils at 182° under 10·5 mm. pressure.

When boiled with 14 per cent. sulphuric acid, the glycol yields *iso*propyl*iso*butenylbenzene, $CMe_2{:}CH\cdot C_6H_4\cdot C_3H_7$, which boils at 105—106° under 10 mm. pressure (Perkin, Trans., 1879, 35, 136), and a *methylene ether* of the glycol, $C_6H_4Pr^{\beta}\cdot CH{<}{\substack{CMe_2\cdot CH_2 \\ O\text{——}CH_2}}{>}O$. This ether can be formed also by the action of formaldehyde on the glycol in presence of hydrochloric acid; it is a colourless oil which boils at 155—159° under 10 mm. pressure. G. Y.

[Chemical Action of Light.] Correction. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1903, 36, 1953. Compare this vol., i, 562).—Triphenylglycol has previously been prepared by Gardeur (Abstr., 1898, i, 436). J. J. S.

Action of Anhydrous Ferric Chloride in the Friedel and Craft's Synthesis. JACOB BOESEKEN (*Rec. trav. chim.*, 1903, 22, 315—317. Compare Abstr., 1901, i, 474, and Nencki, Abstr., 1899, i, 879).—When benzoyl chloride is boiled with anhydrous ferric chloride (1 mol.) and an excess of carbon disulphide, scarlet-red, hygroscopic crystals having the composition $BzCl,FeCl_3$ separate; these, on being boiled with benzene, give yellowish-brown crystals of the *compound* $COPh_2,FeCl_3$, which is easily decomposed by water forming benzophenone. The action of ferric chloride is therefore precisely similar to that of aluminium chloride in the Friedel and Craft's reaction. W. A. D.

Permanganates as Oxidising Agents. FRITZ ULLMANN and J. BEX UZBACHIAN (*Ber.*, 1903, 36, 1797—1807).—Unlike potassium permanganate, which leaves potassium hydroxide in solution when used as an oxidising agent, calcium permanganate leaves only the neutral insoluble manganate. In only a few instances, however, does it give a better yield than the potassium salt. Methods are given of preparing benzoic acid, *iso*phthalic acid, benzene-1 : 3 : 5-tricarboxylic acid, 4-*chlorobenzene*-1 : 3-*dicarboxylic acid* (white needles, melting at 294·5°), 2-nitrobenzoic acid, 2-, 3- and 4-acetylaminobenzoic acids, 5-nitro-2-acetylaminobenzoic acid (m. p. 221°; the amino-acid melts at 269·5°), 2 : 4-*diacetylaminobenzoic acid* (white needles, m. p. 261°; the *diamino*-acid forms unstable, colourless crystals and melts irregularly at about 140°; its *hydrochloride* decomposes above 200°), 4-acetylamino*iso*phthalic acid (m. p. 289·5°; the *dimethyl* ester forms colourless crystals and melts at 126°), 3-methoxybenzoic acid, phthalonic and

phthalic acids, 2-*formylmethylaminobenzoic acid* (colourless flakes, m. p. 168·5—169°), 2-*formylethylaminobenzoic acid* (m. p. 119·5°), and carbamide (from KCN). In many cases, the yields are increased by the addition of magnesium sulphate or of carbon dioxide, by using calcium permanganate, or by working at a low temperature with very dilute permanganate. T. M. L.

Preparation of Phenylglycinethioamide-*o*-carboxylic Esters. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 141698. Compare D.R.-P. 136779, and Bernthsen, Abstr., 1878, 788).—*Methyl phenylglycinethioamide-*o*-carboxylate,* $NH_2·CS·CH_2·NH·C_6H_4·CO_2Me$, prepared by saturating an alcoholic suspension of methyl-ω-cyanomethylanthranilate with hydrogen sulphide, melts at 178° after crystallisation from benzene. The *ethyl ester* melts at 188°. C. H. D.

The Isomeric β-Hydroxysulphonaphthoic Acids L and S, and the Determination of their Structure by the "Sulphite Method." HANS BUCHERER (*Zeit. Farb. Text. Chem.*, 1903, 2, 193—199).—The acid S, which has formerly been considered as the more sparingly soluble one, is in reality only so in concentrated, or in 50 per cent., sulphuric acid; it is more soluble in water or very dilute sulphuric acid than the L acid, and its calcium and sodium salts are more easily soluble than those of the latter substance. That the S acid has the structure $[OH : CO_2H : SO_3H = 2 : 3 : 8]$ and the L acid the structure $[OH : CO_2H : SO_3H = 2 : 3 : 6]$ is shown as follows.

The L acid, when heated with sodium hydrogen sulphite (compare German Patents, 115335, 117471, and 122570), loses carbon dioxide and gives 2-naphthol-6-sulphonic acid (or its sulphurous acid derivative); with ammonium sulphite and ammonia at 125°, it forms 2-naphthylamine-6-sulphonic acid, and with the sulphite and aniline it gives 2-phenylnaphthylamine-6-sulphonic acid. The S acid, when treated similarly, gives 2-naphthol-, 2-naphthylamine-, and 2-phenylnaphthylamine-8-sulphonic acids. W. A. D.

Preparation of a *cyclo*Geraniolenecarboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 141699).—Dihydro*iso*phorone combines with hydrogen cyanide to form *dihydro*iso*phoronecyanohydrin*, $CMe_2{<}{\begin{matrix}CH_2·C(OH)(CN)\\CH_2\text{———}CHMe\end{matrix}}{>}CH_2$, a viscous oil which breaks up into its components when heated, and is hydrolysed by mineral acids, forming cis-*hydroxydihydro*iso*phorylcarboxylic acid*, melting at 113°, and the *trans*-acid, melting at 130°, which are mutually convertible. The cyanohydrin forms an oily *acetyl* derivative boiling at 146° under 17 mm. pressure, which, by cold concentrated sulphuric acid, is converted into a mixture of cis-*hydroxydihydro*iso*phorylcarboxylamide*, $CMe_2{<}{\begin{matrix}CH_2·C(OH)(CONH_2)\\CH_2\text{————}CHMe\end{matrix}}{>}CH_2$, crystallising from benzene in silky needles melting at 128—129° and boiling at 190° under 15 mm. pressure, and the trans-*amide*, crystallising from alcohol in prisms or leaflets melting at 196° and boiling at 210° under 38 mm. pressure. The amides yield the hydroxy-acids on further hydrolysis. On distil-

ling the mixed amides with potassium hydrogen sulphate under 14 mm. pressure, a colourless oil passes over at 170—175° and solidifies on cooling. When fractionally distilled, this yields cyclo*geraniolenenitrile*, $CMe_2<\begin{matrix}CH_2\cdot C(CN)\\ CH_2\cdot CHMe\end{matrix}>CH$ or $CMe_2<\begin{matrix}CH{=}C(CN)\\ CH_2\cdot CHMe\end{matrix}>CH_2$, a colourless oil with an odour of peppermint, boiling at 117° under 14 mm. pressure and at 220—221° under 760 mm. pressure, and cyclo*geraniolenecarboxylamide*, which crystallises from benzene in glistening needles and boils at 168° under 11 mm. pressure. When boiled with alcoholic potassium hydroxide, the amide is converted into cyclo*geraniolenecarboxylic acid*, $CMe_2<\begin{matrix}CH{:}C(CO_2H)\\ CH_2{-}CHMe\end{matrix}>CH_2$ or $CMe_2<\begin{matrix}CH_2\cdot C(CO_2H)\\ CH_2{-}CHMe\end{matrix}>CH$, which crystallises from benzene in prisms and needles, melts at 140°, boils at 154° under 16 mm. pressure, and dissolves in alcohol, ether, or light petroleum. A solution of the sodium salt decolorises potassium permanganate. The melting points of the acid and amide are not sharp, even after repeated crystallisation, and a mixture of the structural isomerides indicated by the formulæ is therefore assumed to be present. C. H. D.

Influence of the Introduction of Unsaturated Radicles on the Rotatory Power of Active Molecules. α-Allyl and Propyl Esters of 4-Methyl-2-*cyclo*pentanonecarboxylic Acid. ALBIN HALLER and MARCEL DESFONTAINES (*Compt. rend.*, 1903, **136**, 1613—1616. Compare this vol., i, 563).—Ethyl β-methyladipate, obtained by the oxidation of pulegone, boils at 138—141° under 15 mm. pressure and has $[\alpha]_D$ +2°30′. When treated in toluene solution with sodium, it gives ethyl 4-methyl-2-*cyclo*pentanonecarboxylate, which boils at 118° under 18 mm. pressure and has $[\alpha]_D$ + 82°20′; it gives a violet coloration with ferric chloride in alcoholic solution. When treated with sodium in ethereal solution, it gives the sodium derivative which, on warming with allyl iodide, gives *ethyl* 4-*methyl*-1-*allyl*-2-cyclo*pentanone-2-carboxylate*, $\begin{matrix}CH_2{-\!-}CO\\ CHMe\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CH{:}CH_2\\ CO_2Et\end{matrix}$, which boils at 139—141° under 18 mm. pressure and has an aromatic odour. In alcoholic solution, it gives a faint violet coloration with ferric chloride; it has $[\alpha]_D$ +62°54′. When sodium ethoxide acts on a mixture of ethyl 4-methyl-2-*cyclo*pentanonecarboxylate and allyl iodide, the product consists of β-methyl-δ-allyladipic acid and its normal and acid esters:

$$\begin{matrix}CH_2{-\!-}CO\\ CHMe\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CH{:}CH_2\\ CO_2Et\end{matrix} + EtOH =$$
$$CO_2Et\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CH{:}CH_2.$$

β-Methyl-δ-allyl-(or *δ-methyl-α-allyl-*)*adipic acid* crystallises in white needles, melts at 100°, and boils at 235° under 20 mm. pressure. In alcoholic solution, it has $[\alpha]_D$ +2°50′. Its diethyl ester boils at 155° under 17 mm. pressure, and has $[\alpha]_D$ +4°24′.

In order to ascertain the influence of the unsaturated allyl group, *ethyl* 4-*methyl*-1-n-*propyl*-2-cyclo*pentanonecarboxylate*,

$$\begin{matrix}CH_2{-\!-}CO\\ CHMe\cdot CH_2\end{matrix}>CPr^{\alpha}\cdot CO_2Et,$$

was prepared. It was obtained in the same way as the corresponding allyl compound; it boils at 136—137° under a pressure of 17 mm. and has $[\alpha]_D$ +51°8′.

These results show that the transformation of an active aliphatic molecule (β-methyladipic ester) into a cyclic molecule is accompanied by a large increase in the rotatory power, and the converse is also true. The introduction of the propyl or allyl radicles into ethyl 4-methyl-2-*cyclo*pentanonecarboxylate decreases the rotatory power, but the rotation of the allyl derivative is superior to that of the propyl compound, and this may be attributed to the presence of the double linking. The substitution of a hydrogen atom of the cyclic ester by the allyl radicle can be more easily effected than substitution by the propyl group.

Some experiments seem to show that the influence of the double linking in increasing the rotatory power diminishes as the double linking recedes from the asymmetric carbon atom, so that allylcamphor, $C_{10}H_{15}O\cdot CH_2\cdot CH\colon CH_2$, has probably a lower rotatory power than propenylcamphor, $C_{10}H_{15}O\cdot CH\colon CH\cdot CH_3$, which is again lower than that of propylidenecamphor, $C_{10}H_{14}O\colon CH\cdot CH_2\cdot CH_3$. J. McC.

Phenylglycollic Acid. William Œchsner de Coninck (*Compt. rend.*, 1903, 136, 1469—1470. Compare this vol., i, 457).—Hydrated phenylglycollic acid melts at 117—118°, and the anhydrous acid at 132—133°. Beyond this temperature the acid partially sublimes; at 185—190°, it is a limpid liquid, at 210° it begins to boil, and at 220° decomposition commences with the formation of carbon monoxide and dioxide, the evolution of these gases becoming more rapid with further increase in temperature. The residue is a viscous, yellow substance having the odour of benzaldehyde, of which it is probably a polymeride, since, on further heating, small quantities of this substance are produced.

When sulphuric acid is added to an aqueous solution of phenylglycollic acid, a violet coloration changing to brown is produced, and an odour of benzaldehyde is developed. Nitric acid gives no coloration with phenylglycollic acid, but after a short time the odour of benzaldehyde becomes apparent and, finally, a small quantity of benzoic acid is formed. T. A. H.

Action of Phosphorus Pentachloride on Ethyl Propionylphenylacetate. Otto Dimroth and Heinrich Feuchter (*Ber.*, 1903, 36, 2238—2251).—According to van't Hoff, compounds of the type $CH_2\colon C\colon CH_2$, where the four hydrogen atoms are replaced by different radicals, or of the type $R_1R_2C\colon C\colon CR_1R_2$, ought to exhibit isomerism of such a nature that the optically inactive variety is resolvable into the *d*- and *l*-enantiomorphs. The research was undertaken with the initial view of preparing such compounds.

Propionylbenzyl cyanide [cyanobenzyl ethyl ketone], prepared by condensing ethyl propionate with benzyl cyanide, crystallises from dilute alcohol in needles which melt at 70°. It dissolves at once in dilute alkalis, whilst its alcoholic solution yields a copper salt with copper acetate. It gives a coloration with ferric chloride, and is

probably the enolic variety. The properties do not agree with those described by Walther and Schickler (Abstr., 1897, i, 524), according to whom the melting point is 58°. *Ethyl propionylphenylacetate*, prepared from the cyanide by converting it into the corresponding imino-ether and then decomposing the latter with water and alcohol, boils at 154—156° under 18 mm. pressure; it is readily soluble in sodium hydroxide solution, forms a copper salt, and, when dissolved in alcohol, gives a deep violet coloration with ferric chloride. It condenses with phenylhydrazine to form 1 : 4-*diphenyl*-3-*ethylpyrazolone*, $NPh<\begin{matrix}CO\cdot CHPh \\ N{=}CEt\end{matrix}$, melting at 197°.

When hydrogen chloride is passed into propionylbenzyl cyanide dissolved in ether and alcohol and the mixture then heated on the water-bath, the imino-ether hydrochloride decomposes and forms ethyl chloride and *propionylphenylacetamide*, which forms colourless crystals melting at 114—116° and gives, in alcoholic solution, an intensely violet coloration with ferric chloride.

The action of phosphorus pentachloride on propionylphenylacetates is represented thus:

$$CH_2Me\cdot CO\cdot CHPh\cdot CO_2R \rightarrow CH_2Me\cdot CCl_2\cdot CHPh\cdot CO_2R \rightarrow$$
$$\rightarrow CH_2Me\cdot CCl{:}CPh\cdot CO_2R \text{ and } CHMe{:}CCl\cdot CHPh\cdot CO_2R.$$

With the latter change may be compared the observations of Fittig on the formation of unsaturated acids from β-halogen- and β-hydroxy-acids.

The mixture resulting from the action of phosphorus pentachloride was treated with water. Under the influence of the resulting hydrogen chloride, *ethyl* β-*chloro*-α-*phenyl*-$\Delta^{\alpha\beta}$-*pentenecarboxylate* is readily hydrolysed with evolution of ethyl chloride, whilst *ethyl* β-*chloro*-α-*phenyl*-$\Delta^{\beta,\gamma}$-*pentene carboxylate* remains unattacked, and is easily separated from unchanged propionylphenylacetate by boiling for several hours with hydrochloric acid; it is a strongly refracting liquid boiling at 159—161° under 18 mm. pressure, and, when acted on by alcoholic potassium hydroxide solution or by sodium ethoxide, does not yield the phenylmethylallenecarboxylic acid desired, the chlorine atom being replaced by an ethoxyl group.

β-*Ethoxy*-α-*phenyl*-$\Delta^{\beta,\gamma}$-*pentenecarboxylic acid*,

$$CHMe{:}C(OEt)\cdot CHPh\cdot CO_2H,$$

melts at 86—87° with vigorous evolution of carbon dioxide; it crystallises in six-sided plates containing $1H_2O$ and is unstable in air. The coloration of its alcoholic solution with ferric chloride appears gradually, becoming after a few minutes intensely violet to brownish-red. The *copper* salt crystallises from light petroleum in stellate needles, melting and decomposing at 115—116°. The position of the double linking in the acid was determined by oxidising it with potassium permanganate to acetaldehyde and ethyl hydrogen phenylmalonate.

The acids resulting from the action of phosphorus pentachloride and ethyl propionylphenylacetate after the hydrolysis with hydrogen chloride were submitted to fractional crystallisation from benzene. β-*Chloro*-α-*phenylpentenecarboxylic acid* ($CH_2Me\cdot CCl{:}CPh\cdot CO_2H$, probably), melting at 121°, was isolated; it crystallises from benzene in silky

needles, which lose their lustre on exposure to air. It is very stable towards potassium permanganate. By the action on it of alcoholic potassium hydroxide solution or of sodium ethoxide, three distinct *ethoxy*-acids were obtained; the first crystallises in glistening leaflets melting at 92°, the second in transparent, six-sided plates melting at 92—93°, and the third in long, silky needles melting at 108°. The acids were further characterised by conversion into their copper salts. On oxidation with potassium permanganate, the three acids yielded the same products, namely, benzoylformic acid and ethyl propionate, thus: $CH_2Me{\cdot}C(OEt){:}CPh{\cdot}CO_2H \rightarrow COPh{\cdot}CO_2H + CH_2Me{\cdot}CO_2Et$. The three acids therefore behave as if they possess the $\alpha\beta$-structure.

A. McK.

Carbon Monoxide Scission from Ethyl α-Bromopropionylphenyl Acetate. OTTO DIMROTH and HEINRICH FEUCHTER (*Ber.*, 1903, 36, 2251—2256. Compare preceding abstract).—When phosphorus pentabromide acts on ethyl propionylphenylacetate, the ketonic oxygen is not replaced by bromine, but the action is identical with that either of the tribromide or of bromine itself; ethyl α-bromopropionylphenylacetate is first formed and then suffers intramolecular rearrangement to ethyl γ-bromopropionylphenylacetate, thus: $CH_2Me{\cdot}CO{\cdot}CPhBr{\cdot}CO_2Et \rightarrow CHBrMe{\cdot}CO{\cdot}CHPh{\cdot}CO_2Et$.

During steam distillation, the former compound loses carbon monoxide to form ethyl methylatropate, whilst the latter forms 1-phenyl-3-methyltetronic acid.

In the preparation of *ethyl methylatropate* from ethyl propionylphenylacetate, the bromination must be conducted at 0° and the product at once further manipulated to prevent the transformation of the α-ester. After the bromination, the mixture is neutralised by a calculated amount of sodium carbonate and then distilled in steam. A vigorous evolution of carbon monoxide takes place and ethyl methylatropate distils over. The action is represented by

$$CH_2Me{\cdot}CO{\cdot}CBrPh{\cdot}CO_2Et = HBr + CO + CHMe{:}CPh{\cdot}CO_2Et.$$

Ethyl methylatropate boils at 128—131° under 15 mm. pressure and on hydrolysis gives methylatropic acid melting at 135—136°; when the latter is oxidised by potassium permanganate, acetaldehyde and benzoylformic acid are produced.

In the preparation of 1-*phenyl*-3-*methyltetronic acid* from ethyl propionylphenylacetate, the product of the reaction must, after the bromination, be submitted to the action of hydrogen bromide for some time in order that the conversion of the α- into the γ-bromo-ester may be as complete as possible. The γ-bromopropionylphenylacetate was identified by its conversion through distillation with steam into the lactone, 1-phenyl-3-methyltetronic acid, $\begin{matrix} CO{\cdot}CHMe \\ | \\ CHPh{\cdot}CO \end{matrix}\!\!>\!O$ (or the corresponding enolic form), which forms hard, glistening crystals melting at 178°. It gives characteristic colour reactions with ferric chloride. Its *benzoyl* compound melts at 100°. 1-Phenyl-3-methyltetronic acid, when boiled with baryta water, is converted into phenylacetic and lactic acids.

A. McK.

Preparation of Indoxyl. DEUTSCHE GOLD- & SILBER-SCHEIDE-ANSTALT VORM. ROESSLER (D.R.-P. 141749).—Phenylglycine is converted into indoxyl by fusion with sodamide (compare D.R.-P 137955). The same reaction takes place with phenylglycinephenylglycide, $NHPh\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot CO_2H$. The fusion is carried out at 200°, alkali hydroxides or cyanides being added to moderate the reaction. Homologues of indoxyl may be prepared in similar manner.

C. H. D.

Derivatives of β-Naphthalene-indigotin. HERMANN WICHELHAUS (*Ber.*, 1903, 36, 1736—1739. Compare Abstr., 1894, i, 42).—β-Naphthisatin is oxidised by chromic acid to *β-naphthisatoic anhydride*, $C_{10}H_6<\begin{matrix}CO-O\\NH\cdot CO\end{matrix}$, which separates from acetone in coarse, pale red crystals, melting and blackening at 264°. *β-Naphthisatinphenylhydrazone* crystallises from alcohol in glistening, orange leaflets, which melt at about 220°, but darken 10° lower. *Acetyl-β-naphthisatin* crystallises from benzene in yellow leaflets with golden lustre, melting at 195°, and dissolving readily in chloroform, less readily in alcohol. *β-Naphthisatoxime* forms yellow leaflets which melt and decompose at 186°, dissolve in alkalis to a yellow solution, and are only slightly soluble in alcohol. *Dimethylaniline-β-naphthisatin* separates from alcohol in white crystals which melt at 280° and dissolve in benzene or chloroform, but not in ether or light petroleum, and only slightly in alcohol. *Phenol-β-naphthisatin* forms white crystals which are soluble in alcohol, insoluble in benzene, ether, or chloroform. *Thiophenol-β-naphthisatin* crystallises from light petroleum in white needles which decompose at 105°. *Piperidyl-β-naphthisatin* forms pale yellow crystals, melts at 140°, and dissolves readily in alcohol. *β-Naphthisatin-β-naphthylhydrazone* melts at 270—272° after crystallisation from benzene, and resembles the phenylhydrazone (compare also Hinsberg, Abstr., 1898, i, 275).

C. H. D.

6-Nitroso-3 : 4-dimethoxybenzoic Acid. CORNELIU SUMULEANU (*Ann. Sci. Univ. Jassy*, 1903, 2, 139—140).—When a solution of 6-nitro-3 : 4-dimethoxybenzaldehyde in benzene is exposed to sunlight for two days, 6-*nitroso*-3 : 4-*dimethoxybenzoic acid*, $NO\cdot C_6H_2(OMe)_2\cdot CO_2H$, is precipitated as a yellow powder ; it darkens at 175°, melts and decomposes at 180—190°, and dissolves in hot alcohol, glacial acetic acid, or acetone, giving green solutions.

W. A. D.

Addition of Ethyl Malonate to αβ-Unsaturated Ketones and Acid Esters. DANIEL VORLÄNDER (*Ber.*, 1903, 36, 2339—2340. Compare Abstr., 1897, i, 272).—By conversion of cinnamenylhydroresorcinol into *cinnamenylglutaric acid*, $CHPh:CH\cdot CH(CH_2\cdot CO_2H)_2$, the addition of ethyl malonate to the αβ-position of the complex $\overset{\delta}{C}:\overset{\gamma}{C}\cdot\overset{\beta}{C}:\overset{\alpha}{C}\cdot CO$ is proved. In presence of excess of ethyl sodiomalonate, a second molecule is not added at the γ-δ-double linking. The acid

melts at 135°, the *anhydride* at 138°, the *methyl* ester at 70°, and the *anilide* at about 142°. E. F. A.

Derivatives and Constitution of Bismuthogallic Acid. PAUL THIBAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 531—535).—*Bismuthogallamide*, $C_7H_4O_5Bi{\cdot}NH_2,H_2O$, prepared by the action of liquefied ammonia on bismuthogallic acid (Abstr., 1902, i, 101), is a reddish-brown, crystalline, hygroscopic powder which decomposes at 160°, has a sp. gr. 2·53 at 15°, and is soluble in acids and alkalis, but insoluble in neutral solvents. When heated with water in closed tubes at 150—200°, it is converted into *ammonium bismuthogallate*.

Bismuthogallanilide, obtained by heating the acid with aniline, resembles the amide in appearance, decomposes at 200°, has a sp. gr. 3·24 at 0°, and is soluble in acids, but not in neutral solvents. It is decomposed when heated in closed tubes with water at 140°. When hydrated bismuth oxide (Abstr., 1900, ii, 106) is heated with an aqueous solution of gallanilide, the hydrated bismuthogallanilide described by Cazeneuve (Abstr., 1893, i, 643) is formed.

Bismuthogallo-o-*toluidide*, similarly prepared, is a brown, crystalline powder which decomposes at 200°, has a sp. gr. 2·62 at 15°, and is decomposed by water in closed tubes at 140°.

The formation of these derivatives is in harmony with the formula $CO_2H{\cdot}C_6H_2(OH){<}^{O}_{O}{>}Bi{\cdot}OH$, ascribed independently by Prunier and by Richard to bismuthogallic acid, and also with that now proposed by the author, $CO_2H{\cdot}C_6H_2(OH)_2{\cdot}O{\cdot}BiO$ (compare Abstr., 1902, i, 290). T. A. H.

Compounds of Hexahydric Alcohols with Mononitrobenzaldehydes. ADOLPHE SIMONET (*Bull. Soc. chim.*, 1903, [iii], 29, 503—507. Compare Fischer, Abstr., 1894, 395).—By the interaction of the isomeric nitrobenzaldehydes dissolved in benzene with mannitol, sorbitol, and dulcitol suspended in sulphuric acid (50 per cent.), a series of nitrobenzylidene derivatives of these polyhydric alcohols is obtained.

Tri-m-*nitrobenzylidene-mannitol*, $C_6H_8O_6(CH{\cdot}C_6H_4{\cdot}NO_2)_3$, separates from benzene in colourless, crystalline flocks, is soluble in benzene, less so in warm alcohol or ether, insoluble in water, and melts at 254°. It is not decomposed by acids. p-*Nitrobenzylidene-mannitol*, $C_6H_{12}O_6{:}CH{\cdot}C_6H_4{\cdot}NO_2$, similarly prepared, crystallises in colourless needles, melts at 198·5° (corr.), and is decomposed by warm dilute acids.

Di-m-*nitrobenzylidene-sorbitol*, $C_6H_{10}O_6(CH{\cdot}C_6H_4{\cdot}NO_2)_2$, separates as a white, crystalline powder from warm alcohol, is slightly soluble in warm benzene, insoluble in water, melts at 220° (corr.), and is readily decomposed by warm dilute acids. p-*Nitrobenzylidene-sorbitol*, $C_6H_{12}O_6{:}CH{\cdot}C_6H_4{\cdot}NO_2$, crystallises in colourless needles from alcohol, melts at 204·5° (corr.), is slightly soluble in boiling benzene, insoluble in ether and water, and is decomposed by warm dilute acids.

m-*Nitrobenzylidenedulcitol* separates from nitrobenzene in colourless needles, melts at 256·5° (corr.), is insoluble in the ordinary solvents, but

soluble in warm nitrobenzene. p-*Nitrobenzylidenedulcitol* crystallises from aniline in colourless needles, melts at 186° (corr.), is soluble, when warmed, in aniline or nitrobenzene, but does not crystallise from its solutions in the latter. It is readily decomposed by warm dilute acids.

The rate of formation of these compounds under the conditions stated varies greatly; for instance, the precipitation of tri-*m*-nitrobenzylidenemannitol is complete after 1 hour, whilst the formation of *p*-nitrobenzylidenesorbitol is complete only after 24 hours.

T. A. H.

Oxidation of *o*-Aminobenzaldehyde and its Relation to Benzoxazole. EUGEN BAMBERGER (*Ber.*, 1903, 36, 2042—2055).—It has not been found possible to isolate the *o*-hydroxylaminobenzaldehyde, $HO{\cdot}NH{\cdot}C_6H_4{\cdot}CHO$, which appears to form the first product of the oxidation of *o*-aminophenol by Caro's acid. In all cases, however, the isomeride (this vol., i, 432) is produced, which is now shown to be o-*formylaminophenol*, $HO{\cdot}C_6H_4{\cdot}NH{\cdot}CHO$, since aqueous alkalis convert it, at the ordinary temperature, into *o*-aminophenol and formic acid, whilst benzoyl chloride converts it into dibenzoyl-*o*-aminophenol; when heated, it loses water and gives Ladenburg's benzoxazole,

$$C_6H_4{<}{\substack{N\\O}}{>}CH.$$

In acid solution, the *o*-formylaminophenol is accompanied only by anthranil, which appears to be a direct product of the dehydration of hydroxylaminobenzaldehyde; in presence of magnesia, anthranil is not formed, but *o*-nitrophenol, *o*-aminophenol, and formic acid are produced; when magnesium carbonate is used, anthranil and *o*-azoxybenzoic acid are also produced. Formylaminophenol can be prepared synthetically by heating together formic acid and *o*-aminophenol; the method is similar to that of preparing benzoxazole, but the product is crystallised by cooling instead of being distilled; it can also be prepared by heating benzoxazole with water.

The resemblance between anthranil and benzoxazole is shown by the formulæ $C_6H_4{<}{\substack{N-\\|\\CH}}{>}O$ and $C_6H_4{<}{\substack{N\\O}}{>}CH$, and by their formation from *o*-hydroxylaminobenzaldehyde, and is further indicated by the fact that benzoxazole has a penetrating odour, is very readily volatile with steam, possesses feeble basic properties, and combines with mercuric chloride to form a *compound*, $C_7H_5NO,HgCl_2$, which separates in silky, white needles, softens at 158°, and melts at 168—169°.

T. M. L.

Aminovanillin. CORNELIU SUMULEANU (*Ann. Sci. Univ. Jassy*, 1903, 2, 131—138).—vic.-o-*Aminovanillin*,

$CHO{\cdot}C_6H_2(OMe)(OH){\cdot}NH_2$ [$CHO : NH_2 : OMe : OH = 1 : 2 : 3 : 4$], obtained by reducing the corresponding nitro-compound with ammoniacal ferrous hydroxide, crystallises from water or benzene and melts at 128—129°; the *acetyl* derivative, $CHO{\cdot}C_6H_2(OMe)(OH){\cdot}NHAc$, crystallises from alcohol in slender, yellow needles and melts at 97°.

o-*Aminovanillinphenylhydrazone*, $C_{14}H_{15}O_5N_3$, crystallises from dilute alcohol or acetic acid in long, yellow needles and melts at 165°; o-*aminovanillinoxime*, $C_8H_{10}O_3N_2$, crystallises from benzene in felted needles, melts at 151—152°, and, when diazotised in acid solution, gives *hydroxymethoxyindiazoneoxime*, $OH{\cdot}C_6H_2(OMe){<}\begin{matrix}\text{—C:N·OH}\\ \text{N:N}\end{matrix}$ (compare Bamberger and Demuth, Abstr., 1901, i, 391), which separates from alcohol in long, acicular crystals. This substance dissolves in a solution of an alkali hydroxide, and, on acidifying, vic.-o-*vanillinazoimide*, $OH{\cdot}C_6H_2(OMe)(CHO){\cdot}N_3$, is precipitated; it crystallises from benzene in slender, felted, yellow needles, melts and decomposes at 169°, and, when heated with a concentrated solution of alkali, gives not the corresponding amino-acid, but apparently only vanillin. W. A. D.

Electrochemical Reduction of *m*-Nitroacetophenone and of *m*-Nitrobenzophenone. KARL ELBS and A. WOGRINZ (*Zeit. Elektrochem.*, 1903, 9, 428—431).—A solution of *m*-nitroacetophenone in aqueous alcohol containing sodium acetate is reduced, at a nickel gauze cathode in the cold, to a mixture of *m*-azoxy- and *m*-azo-acetophenone. Further reduction to the corresponding hydrazo-compound is very incomplete. *m*-Nitroacetophenone, dissolved in alcohol containing sulphuric acid and copper sulphate, is reduced to *m*-aminoacetophenone, the same product being obtained in ammoniacal solution. The yield is about 75 per cent. of the theoretical quantity.

m-Nitrobenzophenone, in alkaline solution, gives an almost quantitative yield of the azoxy-compound. When the reduction is carried out at the boiling temperature, the azo-compound is obtained in very good yield. This may be further reduced to the hydrazo-compound, from which the corresponding *m*-dibenzoylbenzidine is obtained. In acid solution, *m*-nitrobenzophenone is readily reduced to the corresponding amino-compound.

In none of the reductions did the carbonyl group take any part in the change. T. E.

Oximes of Unsymmetrical Ketones with Two Similar Nuclei. W. SCHARWIN and SCHORIGIN (*Ber.*, 1903, 36, 2025—2027).—2 : 4′-*Dimethylbenzophenone*, prepared by the Friedel-Craft's reaction from toluene and *o*-toluoyl chloride, boils at 175° under 12 mm. and at 316—318° under the ordinary pressure, has a sp. gr. 1·074 at 19°, and gives only a single *oxime*, which crystallises from alcohol in colourless needles and melts at 122°; as the oxime is converted by the Beckmann transformation into the *p*-toluidide of *o*-toluic acid, it has the configuration

$$(o)\ CH_3{\cdot}C_6H_4{\cdot}\underset{\underset{N\cdot OH}{\|}}{C}{\cdot}C_6H_4{\cdot}CH_3\ (p).$$

On the other hand, the *oxime* of 3 : 4′-dimethylbenzophenone exists in two forms, which can be separated by crystallisation from alcohol, and melt respectively at 143° and 118—119°. 3 : 4′-*Dimethylbenzo-*

phenone crystallises from alcohol in large, transparent prisms, melts at 82°, and boils at 328—330°. W. A. D.

δ-(1 : 5)-Diketones. EMIL KNOEVENAGEL (*Ber.*, 1903, 36, 2118—2123. Compare Rabe and Elze, Abstr., 1902, i, 709).—Most 1 : 5-diketones form bispyrazolones with hydrazine hydrate and react, losing water or alcohol, as diketonic or dienolic compounds; many, however, form only monopyrazolones and have been regarded by Rabe and Elze as *cyclo*hexanolones. They are here considered to be half enols, and it is assumed that in such cases complete enolisation is structurally hindered. The formation of dihydropyridine derivatives from 1 : 5-diketones and ammonia probably necessitates a double enolisation, and in cases where this is structurally hindered, dihydropyridine derivatives are not formed.

The conversion of diketonic into keto-enolic or bisenolic compounds, or the reverse change, would undoubtedly be easily brought about by piperidine, and it is not necessary to assume the formation of a cyclic compound. Further, the conversion of *cyclo*hexenones into pyridine derivatives, the reverse of Hantzsch's conversion of dihydropyridines into *cyclo*hexenones, can take place under certain conditions; so that probably *cyclo*hexanolones would undergo such changes still more easily.

It is thus more feasible to assume the existence of stable non-cyclic keto-enolic compounds in which one half of the molecule reacts entirely as a ketone and the other entirely as an enol.

Thus, ethyl benzylidenebisacetoacetate is keto-enolic,

$$OH{\cdot}CMe{:}C(CO_2Et){\cdot}CHPh{\cdot}CH(CO_2Et){\cdot}CO{\cdot}CH_3,$$

and with ammonia exchanges OH for NH_2 and opposes the greatest resistance to any further enolisation.

Compounds such as ethyl benzylideneacetoacetate, containing the conjugated system $O=C-C=C$, form additive compounds, for example, with β-aminocrotonic acid, thus:

$$HO{\cdot}CMe{:}C(CO_2Et){\cdot}CHPh{\cdot}C(CO_2Et){:}CMe{\cdot}NH_2,$$

which at once lose water and give dihydropyridines.

The following abstracts, together with those on pp. 651, 660, show experimental evidence for these theories. E. F. A.

Action of Ammonia on *cyclo*Hexenone. EMIL KNOEVENAGEL and A. ERLER (*Ber.*, 1903, 36, 2129—2130).—On heating dimethyl*cyclo*hexenone with an equal weight of ammonium carbonate for 6 hours at 130—140°, a small quantity of a base was formed, which proved to be identical with 2 : 4 : 6-trimethylpyridine. This conversion of *cyclo*hexenone into dihydropyridine derivatives is the reverse of Hantzsch's reaction—the formation of *cyclo*hexenone by the action of hydrochloric acid on dihydropyridine (Abstr., 1883, 82).

E. F. A.

Condensation of Benzoylacetone with Benzaldehyde. EMIL KNOEVENAGEL and A. ERLER (*Ber.*, 1903, 36, 2131—2136).—By the interaction of 2 mols. of benzoylacetone and 1 mol. of benzaldehyde dissolved in alcohol in presence of piperidine, two isomeric forms of

benzylidenebisbenzoylacetone are formed. The more stable, or *a*-, form melts at 195°, the labile, *β*-, form melts at 121° and is easily converted in presence of piperidine into the *a*-modification. With ferric chloride, the *β*-form gives a dark red coloration, and is thus probably the enolic modification, whereas the *a*-compound shows no colour reaction. Hydroxylamine hydrochloride converts the *a*-compound almost quantitatively into a crystalline substance melting at 199°, which is probably 5-*oximido-2-acetyl-4-benzoyl-*1 : 3-*diphenyl*cyclo*hexene*. Dry hydrogen chloride acts in a similar manner to form 2-*acetyl-4-benzoyl*-1 : 3-*diphenyl*-cyclo*hexenone*-5, which crystallises from alcohol in yellow needles melting at 183°. When heated with alkali hydroxides, benzylidenebisbenzoylacetone forms a 1 : 3-*diphenyl*cyclo*hexenone*-5, crystallising from light petroleum in white needles melting at 82—83°, and therefore not identical with the compound obtained by Knoevenagel and Schmidt (Abstr., 1895, i, 48), which formed yellow crystals melting at 70—72°. The *phenylhydrazone* forms dark green needles from alcohol and melts at 181°.

Benzylidenebenzoylacetone, CHPh:CBz·COMe, is formed by dissolving benzoylacetone (1 mol.) in benzaldehyde (1 mol.) at 35° and subsequently adding a few drops of piperidine; it crystallises from light petroleum in highly refractive crystals melting at 98—99°. *Ethyl acetoacetate-benzylidenebenzoylacetone*, formed by the condensing action of alcoholic piperidine on its components, melts at 183°. Dry hydrogen chloride converts it into *ethyl* 1 : 3-*diphenyl-2-acetyl*-5-cyclo-*hexenone-4-carboxylate*, which melts at 164°. E. F. A.

Products of the Condensation of Acetylacetone with Aldehydes. EMIL KNOEVENAGEL (with KONRAD BIALON, WALTER RUSCHHAUPT, G. SCHEIDER, FR. CRONER, and W. SÄNGER) (*Ber.*, 1903, **36**, 2136—2180. Compare Abstr., 1895, i, 48).—Acetylacetone combines with benzaldehyde to form benzylidenebisacetylacetone, which, under the influence of hydrogen chloride in alcoholic solution, loses two molecules of water forming phenyldimethyl-*m*-bis*cyclo*hexenone. Slightly varying the experimental conditions by using chloroform as solvent, only one molecule of water is eliminated and 2 : 4-*diacetyl-3-phenyl-1-methyl*-cyclo*hexenone*-5,

$$CH{<}{\substack{CMe\cdot CHAc \\ CO-CHAc}}{>}CHPh,$$

is formed.

This crystallises from light petroleum in transparent, faintly yellow plates melting at 68°, and when heated with hydroxylamine hydrochloride forms a compound, $C_{17}H_{18}O_2N_2$, crystallising in white prisms and melting at 103—105°. This is probably a *dioxime* of *dimethylphenyl*-m-*bis*cyclo*hexenone*. In presence of sodium hydroxide, an isomeride melting at 190—193° is obtained.

Boiling with alkali converts the ketone into dimethylphenyl-*m*-bis-*cyclo*hexenone, which can be distilled unchanged at 355° under the ordinary pressure, and when treated with hydroxylamine is converted into a mixture of mono- and di-oximes; the latter melts at 193° and is identical with that just described.

Phenylhydrazine yields a *monophenylhydrazone*, which forms dark reddish-yellow crystals melting at 199°.

Acetylacetone and acetaldehyde combine, in presence of piperidine, to form *ethylidenebisacetylacetone*, which crystallises in large, transparent prisms melting at 108°. Aqueous hydrochloric acid converts it into *trimethyl*-m-*bis*cyclo*hexenone*. Two isomerides are simultaneously formed; one crystallises in plates from alcohol, is soluble in water, but insoluble in ether and light petroleum, melts at 136°, and boils without decomposition at 320°. The other is soluble in light petroleum or ether, insoluble in water, melts at 64°, and boils unchanged at 280°. Dry hydrogen chloride in chloroform solution forms this isomeride only. These substances are also obtained on distilling ethylidenebisacetylacetone in a vacuum.

Acetylacetone and ethyl benzylideneacetoacetate condense in presence of diethylamine to form a compound $C_{18}H_{22}O_5$, *ethyl acetylacetonebenzylideneacetoacetate*, melting at 123°, which is an isomeride of the compound melting at 156°, described by Knoevenagel and Werner (Abstr., 1895, i, 48). The nature of this isomerisation has not been established.

Acetylacetone (2 mols.) condenses with formaldehyde in presence of either piperidine or diethylamine to a solid and a liquid modification of *methylenebisacetylacetone*, $OH\cdot CMe\colon C(COMe)\cdot CH_2\cdot CH(COMe)_2$; the solid melts at 87—88° and gives a dark violet coloration with ferric chloride in alcoholic solution, but forms no dihydropyridine derivative with ammonia.

The liquid modification gives a coloration with ferric chloride, forms diacetyldihydrolutidine with ammonia and a bisdimethylpyrazole with hydrazine hydrate, and is probably the dienolic form,

$$CH_2[C(COMe)\colon CMe\cdot OH]_2.$$

Methylenebisacetylacetone, when acted on by hydrogen chloride in chloroform solution, forms a compound, $C_{11}H_{14}O_3$, which melts at 75° and gives a dark red coloration with ferric chloride. It is thus the enolic form of 2 : 4-*diacetyl*-1-*methyl*cyclo*hexenone*-5,

$$CH_2\begin{matrix}\diagup CH(COMe)\cdot CMe \diagdown \\ \diagdown CH(COMe)—CO \diagup\end{matrix}CH.$$

From this, by the action of ammonia, a yellow, crystalline substance, $C_{11}H_{15}O_2N$, is formed, melting at 136°; the *platinichloride* melts at 225—230°.

Methylenebisacetylacetone, under the influence of concentrated sulphuric acid, loses two molecules of water, forming *dimethyl*-m-*bis*cyclo*hexenone*; this melts at 125—127° and is easily soluble in most organic solvents.

Strong hydrochloric acid, on the other hand, converts methylenebisacetylacetone into 4 : 6-diacetyl-*m*-cresol, the *dioxime* of which melts at 191°.

Acetylacetone and formaldehyde, when condensed in molecular proportions, do not form methyleneacetylacetone, but a product composed of two molecules of each less a molecule of water,

$$CH(COMe)_2\cdot CH_2\cdot C(COMe)_2\cdot CH_2\cdot OH.$$

This *methylolmethylenebisacetylacetone* melts at 91°.

Under the influence of hydrogen chloride, it yields a cyclic compound, 2 : 4-*diacetyl*-4-*methylol*-1-*methyl*cyclo*hexenone*-5, melting at 69°, whilst with hydroxylamine it forms a substance, $C_{11}H_{14}O_2N_2$, crystallising in colourless needles and melting at 141—142°, which is exceedingly stable towards acids, and is probably *methylenebis*-3 : 5-*dimethyl*iso*oxazole*. This is also obtained from the *cyclo*hexone.

Dimethylolmethylenebisacetylacetone, $C_{13}H_{20}O_6$, formed by the condensation of acetylacetone with 6 molecules of formaldehyde, crystallises with $2H_2O$ and melts at 95°, or when anhydrous, at 129°. Its *dioxime* crystallises with $1H_2O$ and melts at 252°. Dry hydrogen chloride converts it into the cyclic derivative, 2 : 4-*diacetyl*-2 : 4-*dimethylol*-1-*methyl*cyclo*hexenone*-5 ; this melts at 145° and forms a *dioxime* melting at 268°.

*Trimethyloldiacetylmethyl*cyclo*hexenone* is also formed in the above condensation. It crystallises from benzene in needles melting at 122°, or from alcohol with water of crystallisation, then melting at 110°. Hydroxylamine converts it into the *iso*oxazole, melting at 142°, described above.

Two other compounds are formed in small quantities during the condensation, namely :

Dimethyloldimethylenetrisacetylacetone, $C_{17}H_{26}O_7$, derived from 3 molecules of acetylacetone and 4 mols. of formaldehyde, less 2 mols. of water, melts at 168°.

Dimethylenetriacetylacetone is derived from 3 molecules of acetylacetone and 2 mols. of formaldehyde, less 2 mols. of water ; it melts at 121°. E. F. A.

Thiobenzoylacetone. VICTOR VAILLANT (*Bull. Soc. chim.*, 1903, iii, 29, 528—530. Compare Abstr., 1899, i, 599).—When sulphur dichloride reacts with the copper derivative of benzoylacetone, dissolved in chloroform, *thiobenzoylacetone*, $S(CHAcBz)_2$, is produced ; this forms slightly yellow, orthorhombic crystals, melts at 95°, is readily soluble in organic solvents with the exception of alcohol, and is insoluble in water. It solutions are neutral to litmus and phenolphthalein. The *sodium* derivative, prepared by adding sodium ethoxide to the ketone dissolved in ether, is a voluminous, pale yellow powder ; the *copper* derivative is a dirty-green, amorphous substance which blackens in presence of moisture ; the *ferric* derivative is brown and forms a deep red solution in alcohol. The *ammonium* derivative is precipitated as a pale yellow powder when ammonia is passed into thiobenzoylacetone dissolved in ether. Similar compounds obtained with various metals are described in the original. T. A. H.

Diphenylquinomethane—the Chromogen of Oxytriphenylmethane Dyes. AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1903, 36, 2333—2339).—p-*Methoxytriphenylchloromethane*, $CPh_2Cl\cdot C_6H_4\cdot OMe$, produced by the action of dry hydrogen chloride on an ethereal solution of the carbinol, crystallises in colourless, flat plates melting at 122—123°. When heated at 180—200°, it evolves methyl chloride and forms a compound, $C_{19}H_{14}O$, of molecular weight about 270, which

crystallises from benzene in brownish-yellow plates melting at 167—168°. This is probably 7 : 7-*diphenylquinomethane*,

$$CPh_2:C<\begin{matrix}CH:CH\\CH:CH\end{matrix}>CO.$$

It unites with hydrogen very readily, forming *p*-hydroxytriphenylmethane, or with water forming the corresponding carbinol, and is specially interesting as the chromogen of the aurin group. Although itself coloured, it does not dye textile fabrics. E. F. A.

Condensation of Anthraquinone with Phenols. W. SCHARVIN and KUSNEZOF (*Ber.*, 1903, 36, 2020—2025).—*Phenolanthraquinone*, probably $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(C_6H_4\cdot OH)_2$, obtained by heating a mixture of anthraquinone, phenol, and stannic chloride for 6—7 hours at 140°, crystallises from alcohol in small, colourless needles, melts at 308—309°, and at higher temperatures is resolved into its constituents; the *diacetyl* derivative crystallises from alcohol in colourless, silky needles and melts at 244°, and the *dibenzoyl* derivative melts at 224—225°.

Resorcinolanthraquinone, $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>O$, prepared by heating a mixture of zinc chloride, anthraquinone, and resorcinol for 6 hours at 200°, is an amorphous, dark brown powder, which, like phenolanthraquinone, is resolved by heat into its constituents; the *diacetyl* derivative is also amorphous.

The foregoing substances are somewhat similar in structure to phenolphthalein and fluorescein, but are less stable towards heat; both fluorescein and phenolphthalein sublime unchanged under conditions which decompose the anthraquinone derivatives. W. A. D.

Derivatives of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 141575).—α-Alphylaminoanthraquinones containing a hydroxyl group in the ortho-position relatively to the alphylamino-group yield dyes, on oxidation, probably having the constitution of oxazines, such as $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}NH\\O\end{matrix}>C_6H_4$. The preparation of the alphylamino-derivative and conversion into oxazine may be carried out in one process by heating the α-nitrohydroxyanthraquinone with the amine and mercuric oxide. The colour-reactions of the following derivatives and their oxazines are described: 1-*nitro*-2-*hydroxyanthraquinone*, 1-*nitro*-2 : 4-*dihydroxyanthraquinone*, 1-*anilino*-2-*hydroxyanthraquinone*, 1-*anilino*-2-*hydroxy*-3-*nitroanthraquinone*, 1-*anilino*-2 : 4-*dihydroxyanthraquinone*, and 1-p-*toluidino*-2 : 4-*dihydroxyanthraquinone*. C. H. D.

Syntheses in the Naphthacenequinone Series. III. CHRISTIAN DEICHLER and CH. WEIZMANN (*Ber.*, 1903, 36, 2326—2330).—11-*Nitro*-6-*hydroxynaphthacenequinone*, produced by the nitration of 6-hydroxynaphthacenequinone in acetic acid solution, crystallises in yellow needles melting at 274°; it forms a sparingly soluble violet potassium salt.

Dinitro-6-*hydroxynaphthacenequinone*, prepared by direct nitration

for an hour at the temperature of the water-bath, crystallises in yellowish-red crystals melting at 260°.

When reduced with zinc chloride and alkali, the nitro-compound yields the corresponding 11-*amino*-6-*hydroxynaphthacenequinone*, which crystallises from nitrobenzene in black needles with a green metallic lustre. As sodium nitrite converts it into the 6 : 11-dihydroxynaphthacenequinone, $C_6H_4<\begin{matrix}CO\cdot C\cdot C(OH)\\ \| \\ CO\cdot C\cdot C(OH)\end{matrix}>C_6H_4$, the constitution of the nitro- and amino-compounds is established.

The dinitro-compound could not be reduced; zinc chloride and alkali convert it into a compound, $C_{18}H_{11}O_4N$, crystallising in violet-black needles, probably *aminodihydroxynaphthacenequinone*.

The nitration of dihydroxynaphthacenequinone can only be effected by acting on the cold solution in strong sulphuric acid with nitrous fumes. *Dinitro*-6 : 11-*dihydroxynaphthacenequinone* forms reddish-brown crystals, and on reduction yields a *diamino*-compound crystallising from nitrobenzene in dark green, glistening needles. E. F. A.

Euphorbone. W. M. OTTOW (*Arch. Pharm.*, 1903, **241**, 223—240. Compare especially Henke, Abstr., 1887, 72).—The material was obtained by extracting euphorbium with light petroleum. The best crystals were obtained from a solution in light petroleum; they melted at 71°. From methyl alcohol, crusts were obtained melting at 114—115°. The crystals from light petroleum lost about 5·6 per cent. of their weight when heated at 97° under diminished pressure. What remained was found to have the same composition and molecular weight as the crystals from methyl alcohol and from acetone, expressed by the formula $C_{27}H_{44}O$. In 1·1 per cent. chloroform solution, $[\alpha]_D$ was 15·0° at 20°; in 4 per cent. solution, 16·8° at 15°, 16·5° at 20°. Treatment with acetic anhydride led to the formation of an apparently new *substance*, melting at 100—102° and with the empirical composition of a monacetyl derivative; no acetyl group could be detected in it, however. Sodium seems to have no action on euphorbone in boiling alcoholic solution. A *dibromo*-additive product, $C_{27}H_{44}OBr_2$, can be obtained melting at about 81°. Heating, with or without a solvent, alters the melting point of euphorbone and lowers its solubility as a rule. When heated in the air, the substance gains in weight. C. F. B.

Phellandrene. FRIEDRICH W. SEMMLER (*Ber.*, 1903, **36**, 1749—1756).—Crude phellandrene, prepared from eucalyptus oil, contains two isomeric phellandrenes, $C_{10}H_{16}$, together with small quantities of cymene and cineole. On oxidation with potassium permanganate in neutral solution, the terpenes are completely oxidised, and the cymene and cineole may be removed by distillation with steam. The residue consists of a mixture of α-hydroxy-β-*iso*propylglutaric lactone, $C_8H_{12}O_4$, and α-hydroxy-β-*iso*propyladipic acid, $C_9H_{16}O_5$, which may be separated by means of their copper salts. The latter acid is not formed by oxidation of the former by potassium permanganate,

and the two acids must therefore be derived from different isomeric phellandrenes.

n-*Phellandrene*, yielding α-hydroxy-β-*iso*propylglutaric acid on oxidation, must have the constitution $CHPr^{\beta}<^{CH:CH}_{CH_2\cdot CH}>CMe$, and ψ-*phellandrene*, yielding α-hydroxy-β-*iso*propyladipic acid, must have the constitution $CHPr^{\beta}<^{CH=CH}_{CH_2\cdot CH_2}>C:CH_2$. Both isomerides are reduced to dihydrophellandrene, $CHPr^{\beta}<^{CH_2-CH}_{CH_2\cdot CH_2}>CMe$. n-*Phellandrene dibromide*, $CHPr^{\beta}<^{CHBr-CH}_{CH_2\cdot CHBr}>CMe$, is readily converted into cymene by alcoholic potash; ψ-*phellandrene dibromide*,

$$CHPr^{\beta}<^{CHBr\cdot CH}_{CH_2-CH_2}>C\cdot CH_2Br,$$

on the other hand, exchanges one bromine atom for an ethoxyl group, forming $CHPr<^{CH(OEt)\cdot CH}_{CH_2-\!\!-\!\!-CH_2}>C\cdot CH_2Br$.

The two isomeric phellandrenes must form distinct nitrites. The hydrochloride of the diamine, obtained by reduction of phellandrene nitrite in acid solution, has been shown by Wallach (Abstr., 1902, i, 725) to decompose into ammonium chloride and cymene on heating, and must therefore have the constitution

$$CHPr^{\beta}<^{CH(NH_2)-CH}_{CH_2\cdot CH(NH_2)}>CMe,$$

and be derived from *n*-phellandrene, which constitutes the bulk of the crude product. C. H. D.

Thujene. Iwan Kondakoff and V. Skworzoff (*J. pr. Chem.*, 1903, [ii], 67, 573—579. Compare Abstr., 1903, i, 505, and Tschugaeff, Abstr., 1901, i, 38, 601).—Thujene was prepared by the xanthate method from a specimen of thujyl alcohol, which boiled at 98·5—101° under 12 mm. pressure and had a sp. gr. 0·9220 at 20°/4°, n_D 1·46405, and $[\alpha]_D$ +61°5′. On distillation, it yielded five fractions having the physical properties given below:

	A.	A₁.	B.	B₁.	C.
B. p....	147—150°	150—151·5°	151·5—152·5°	152·5—156°	156—168°
Sp. gr.	0·8258 at 18°	0·8260 at 18°	0·8279 at 17°	0·8286 at 17°	0·8286 at 17°
n_D......	1·44929	1·45001	1·44999	1·44909	1·45259
$[\alpha]_D$ ...	+48°32′	+40°15′	+28°12′	+12°1′	+3°33′

These results are compared with those of Tschugaeff and the value of the xanthate method discussed.

The authors reply to the criticisms of Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 81). G. Y.

Varieties of India-rubber. III. Carl D. Harries (*Ber.*, 1903, 36, 1937—1941. Compare this vol., i, 189, and Abstr., 1902, i, 811).—Mozambique rubber and Guayrule rubber, both of which are impure varieties, yield the nitrosite, $C_{20}H_{30}O_{14}N_6$, decomposing at 160—161° Gutta-percha and balata yield nitrosites under similar treatment.

That from gutta-percha is yellow, decomposes at about 160—161°, and seems to have the formula $C_{10}H_{15}O_7N_3$; that from balata decomposes at 155° and its percentage composition does not agree with the above formula.

The formation of the nitrosite may be employed for the estimation of rubber in different preparations. J. J. S.

Natural Resins ["Ueberwallungsharze"]. VIII. Oxidation of Lariciresinol. MAX BAMBERGER and HEINRICH RENEZEDER (*Monatshefte*, 1903, **24**, 209—217. Compare Abstr., 1898, i, 88, and 1899, i, 929).—Tetra-acetyllariciresinol, $C_{17}H_{12}(OMe)_2(OAc)_4$, on careful oxidation with a cold solution of chromic acid in acetic acid, yields a compound, $C_{17}H_{12}O_2(OMe)_2(OAc)_4$, which is hydrolysed by alcoholic potash to a crystalline substance, $C_{17}H_{10}O(OMe)_2(OH)_2$. This melts at 180—181°, is soluble in most organic solvents, gives a red coloration with iron chloride and a blood-red shade with concentrated sulphuric or hydrochloric acids, and reduces ammoniacal silver nitrate solution. It forms a *diacetyl* derivative, insoluble in cold alkali, which crystallises in colourless needles melting at 168°. Methyl sulphate converts it into the *dimethyl ether* melting at 131°. E. F. A.

Cyclamin. FR. PLZÁK (*Ber.*, 1903, **36**, 1761—1765).—Cyclamin, the glucoside of cyclamen-tubers, is extracted by 70 per cent. alcohol and purified by repeated solution in hot alcohol, from which it separates on cooling as a white, amorphous powder which begins to melt at 225°, and has the composition $C_{25}H_{42}O_{12}$. It dissolves slowly in water and is insoluble in ether. The specific rotation of a 2 per cent. solution is $[\alpha]_D$ $-36{\cdot}3°$ at 20°. It does not reduce Fehling's solution.

Cyclamin is hydrolysed when heated with dilute sulphuric or hydrochloric acid, forming an insoluble product, *cyclamiretin*, dextrose, and a pentose, according to the equation $C_{25}H_{42}O_{12} + H_2O = C_{14}H_{22}O_2 + C_6H_{12}O_6 + C_5H_{10}O_5$. The pentose is isolated from the filtrate from cyclamiretin by warming the syrup with alcoholic phenylbenzylhydrazine. *l*-Arabinose is thus isolated, but appears to be derived from a pentosan, which is only removable from cyclamin with great difficulty. Pure cyclamin yields an uncrystallisable pentose, cyclose (compare Rayman, Abstr., 1898, i, 229), having a specific rotation $[\alpha]_D$ $+48{\cdot}78°$ at 20° and forming an osazone which melts at 151°. No hydrazone could be prepared. The strength of the pentose solution was determined by distillation with hydrochloric acid and estimation of the furfural produced, and also by means of Fehling's solution.

The insoluble product, cyclamiretin, appears to be identical with Rochleder's sapogenin. It is an amorphous substance which begins to melt at 215° and is insoluble in water, but readily soluble in alcohol and ether. Analysis indicates the composition $C_{14}H_{22}O_2$.

C. H. D.

Action of Emulsin on Salicin and Amygdalin. Theory of the Action of Emulsin. VICTOR HENRI and S. LALOU (*Compt. rend.*, 1903, **136**, 1693—1694).—The velocities of hydrolysis of salicin and amygdalin by emulsin have been determined and the velocity of

hydrolysis of mixtures of these two glucosides. The hydrolysis was followed polarimetrically.

The results show that the speed of the action of emulsin on a mixture of salicin and amygdalin is less than the sum of the speeds of the action of the same quantity of emulsin on salicin alone and on amygdalin alone. The velocity of hydrolysis in the mixture is greater than that for either of the glucosides alone. The difference between the velocity of the action on the mixture and the sum of the single velocities increases with the concentration of the solution.

These results are best interpreted by assuming that the emulsin first forms an intermediate compound with the glucoside, and this then decomposes, regenerating the ferment. J. McC.

The Phthalones. Alexander Eibner (*Ber.*, 1903, 36, 1860—1861).—A claim for priority (compare von Huber, this vol., i, 576). E. F. A.

Derivatives of Aminopyromucic Acid and of Furfurylamine. R. Marquis (*Compt. rend.*, 1903, 136, 1454—1456).—*Ethyl aminopyromucate*, $NH_2 \cdot C_4OH_2 \cdot CO_2Et$, prepared by the reduction of ethyl nitropyromucate (this vol., i, 50), crystallises in colourless prisms, melts at 95°, and is soluble in organic solvents with the exception of light petroleum and in warm water; it cannot be saponified without complete decomposition. The *acetyl* derivative separates from boiling acetone in colourless leaflets, melts at 173·5°, solidifies on further heating, and re-melts at 177·5°; the latter modification is also produced when the first form is left in contact with its mother liquor; both forms dissolve in dilute alkaline liquids and are reprecipitated by carbon dioxide.

Acetylaminopyromucic acid, $NHAc \cdot C_4OH_2 \cdot CO_2H$, crystallises from acetone in colourless needles, decomposes at 285°, and is sparingly soluble in alcohol and water; the *potassium*, *calcium*, and *copper* salts were prepared. When the acid, dissolved in pyridine, is heated in closed tubes at 170°—180°, *acetylfurfurylamine*, $C_4OH_3 \cdot NHAc$, is formed; this crystallises in slightly yellow leaflets, melts at 112°, is readily soluble, except in benzene and light petroleum, and is completely decomposed by acid and alkali solutions.

Ethyl benzoylaminopyromucate crystallises in colourless needles, melts at 99—100°, is soluble in organic liquids and in dilute alkali solutions, and readily resinifies. T. A. H.

7:8-Dihydroxy-2-methylchromone. M. Blumberg and Stanislaus von Kostanecki (*Ber.*, 1903, 36, 2191—2193).—Gallacetophenone trimethyl ether reacts with ethyl acetate in presence of metallic sodium to form 2 : 3 : 4-*trimethoxybenzoylacetone*,

$$C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3,$$

crystallising from alcohol in white leaflets melting at 65°. Hydriodic acid reduces it to 7 : 8-*dimethoxy-2-methylchromone*,

$$\begin{array}{l} OMe \cdot C{:}C(OMe) \cdot C{-}O{-}CMe \\ \quad\ \ | \qquad\qquad\quad\ \ \| \qquad\ \ \| \\ CH{:}CH{-}{-}C \cdot CO \cdot CH \end{array},$$

which crystallises from hot water in bundles of white needles containing $1H_2O$, and melting at 102° after dehydration. Further heating with hydriodic acid removes the methyl groups, forming 7 : 8-*dihydroxy-2-methylchromone*, which crystallises from boiling water in long, glistening needles containing $\frac{1}{2}H_2O$, melting at about 243° after dehydration, and dissolving in sodium hydroxide to an intensely yellow solution. The alcoholic solution is coloured green by ferric chloride. The *diacetyl* derivative crystallises from dilute alcohol in white needles which melt at 120° (compare also this vol., i, 272).

C. H. D.

Transformation Product of the Parent Substance of Brazilin. Stanislaus von Kostanecki and Lorenzo L. Lloyd (*Ber.*, 1903, **36**, 2193—2199).—The oxidation product of brazilin trimethyl ether (compare Abstr., 1902, i, 481) is reduced successively by hydriodic acid to the compounds $C_{16}H_6O(OH)_4$ and $C_{16}H_7O(OH)_3$. The latter yields a compound $C_{16}H_{10}O$ on distillation with zinc dust. The possible formulæ of the products are discussed at length, and the compound $C_{16}H_{10}O$, or *brazan*, is formulated as *phenylene*-2 : 3-*naphthylene oxide*, $O{<}\begin{matrix}C_6H_4 \\ | \\ C_{10}H_6\end{matrix}$.

2 : 7 : 8 : 5-(or 10)-*Tetrahydroxybrazan*,

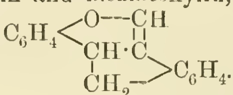
$$\begin{array}{l} OH\cdot C\cdot CH{=}C\cdot O\cdot C\cdot CH{=\!=}C\cdot CH{:}C\cdot OH \\ CH\cdot CH{:}C{-\!-}C\cdot C(OH){:}C\cdot CH{:}C\cdot OH \end{array},$$

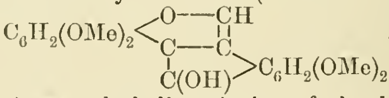
obtained by gentle reduction of the oxidation-product with hydriodic acid, crystallises from dilute alcohol, but discolours in the air; its *tetra-acetyl* derivative melts at 208—209°. The solution in concentrated sulphuric acid is orange with a characteristic green fluorescence. *Tetramethoxybrazan* crystallises from alcohol in white needles, melts at 158°, and dissolves in alcohol with violet fluorescence; it is identical with Herzig's β-tetramethyldehydrobrazilin (Abstr., 1902, i, 482). 2 : 7 : 8-*Trimethoxybrazan*, prepared by further reduction of the tetrahydroxy-compound with hydriodic acid and methylation with methyl sulphate, crystallises from benzene in white leaflets, melts at 244—246°, and dissolves in concentrated sulphuric acid to a violet solution, becoming green on standing. Brazan is obtained by distillation of the tetrahydroxy-derivative, or better, of Bollina, Kostanecki, and Tambor's trihydroxybrazan (Abstr., 1902, i, 482) with zinc dust, and crystallises from alcohol in leaflets melting at 202°. Its alcoholic solution exhibits a greenish-blue fluorescence.

C. H. D.

Coloured Transformation Products of Brazilin. Stanislaus von Kostanecki and Lorenzo L. Lloyd (*Ber.*, 1903, **36**, 2199—2201). —Chromic acid oxidises tetra-acetoxybrazan (compare preceding abstract) in glacial acetic acid solution to 2 : 7 : 8-*triacetoxybrazan-quinone*, $OAc\cdot C_6H_3{<}\begin{matrix}O\cdot C\cdot CO \\ \,\,\,\,\| \\ \,\,\,\,C\cdot CO\end{matrix}{>}C_6H_2(OAc)_2$, which crystallises from glacial acetic acid in small, yellow needles melting at 281°, and dissolving in concentrated sulphuric acid to a green solution. Reduction and simultaneous acetylation by Liebermann's method (Abstr., 1888,

717) converts it into 2 : 5 : 7 : 8 : 10-*penta-acetoxybrazan*, crystallising from acetic acid in colourless needles melting at 268°. 2 : 7 : 8-*Trimethoxybrazanquinone*, prepared by oxidation of 5- (or 10-)hydroxy-2 : 7 : 8-trimethoxybrazan with chromic acid, crystallises from acetic acid in orange-red needles melting at 260° and dissolving in concentrated sulphuric acid to a green solution. Simultaneous reduction and acetylation convert it into 2 : 7 : 8-*trimethoxy*-5 : 10-*diacetoxybrazan*, which crystallises from acetic acid in white needles melting at 254—255°. Hydrolysis with sodium hydroxide and subsequent methylation yields 2 : 5 : 7 : 8 : 10-*pentamethoxybrazan*, melting at 167°. C. H. D.

Naphthalene from the Transformation Products of Hæmatoxylin. STANISLAUS VON KOSTANECKI and A. ROST (*Ber.*, 1903, 36, 2202—2206).—The name "rufen" is proposed for benzylchromene, the parent substance of brazilin and hæmatoxylin, and "rufindan" for the hypothetical compound 

Perkin's tetramethylhæmatoxylon, obtained by oxidation of hæmatoxylin tetramethyl ether (Trans., 1902, 81, 1059), is not a ketone, but a diol, being 1 : 2 : 8 : 9-tetramethoxyrufindandiol (compare Kostanecki and Lampe, Abstr., 1902, i, 481). When acetylated and hydrolysed, it yields 1 : 2 : 8 : 9-tetramethoxyrufindenol (Perkin's anhydrotetramethylhæmatoxylon),  . On addition of sulphuric acid to an alcoholic solution of the diol, water is eliminated, and 5-(or 10-)*hydroxy*-1 : 2 : 7 : 8-*tetramethoxybrazan* is produced (compare the trimethoxy-compound in preceding abstract), crystallising from benzene in leaflets which melt at 218°. The *acetyl* derivative crystallises from alcohol and acetic acid in rosettes of needles melting at 196°. Methylation yields 1 : 2 : 5(or 10) : 7 : 8-*pentamethoxybrazan*, crystallising from alcohol in white needles and melting at 174°. Chromic acid oxidises the tetramethoxy-compound to 1 : 2 : 7 : 8-*tetramethoxybrazanquinone*, which crystallises from acetic acid and alcohol in claret-red needles melting at 264° and dissolving in concentrated sulphuric acid to an olive-green solution. Simultaneous reduction and acetylation converts it into 1 : 2 : 7 : 8-*tetramethoxy*-5 : 10-*diacetoxybrazan* melting at 234°.

Hydroxytetramethoxybrazan and tetramethoxybrazanquinone yield naphthalene on distillation with zinc dust. C. H. D.

Some New Compounds of the Pyranol Series. ROBERT FOSSE and A. ROBYN (*Compt. rend.*, 1903, 136, 1566—1569. Compare Abstr., 1902, i, 449; this vol., i, 49, 357, 510).—The oxidising power of the pyryl salts on alcohol has been made use of for the production of some pyrones.

1 : 8-*Dimethyl*-4 : 5-*di*iso*propylxanthone*,

$$\begin{array}{l} \mathrm{CH\cdot CMe{:}C\cdot CO\cdot C{:}CMe{-}CH} \\ \mathrm{CH\cdot CPr^{\beta}{:}C{-}O{-}C{:}CPr^{\beta}\cdot CH} \end{array},$$

was obtained by starting with thymol; it melts at 121°. If this compound is subjected in alcohol solution to the action of nascent hydrogen until the residue left when the alcohol is evaporated is soluble in warm hydrochloric acid, the pyranol is produced. When the pyranol is dissolved in warm hydrochloric acid, a pyryl salt is formed,

$$C_6H_2MePr^{\beta}<\underset{O}{\overset{CH(OH)}{}}>C_6H_2MePr^{\beta} + HCl =$$

$$C_6H_2MePr^{\beta}<\underset{OCl}{\overset{CH}{|}}>C_6H_2MePr^{\beta},$$

and when the red solution is poured into alcohol, decolorisation takes place, aldehyde is evolved, and 1 : 8 *dimethyl*-4 : 5-*di*iso*propylxanthene*, $C_6H_2MePr^{\beta}<\underset{O}{\overset{CH_2}{}}>C_6H_2MePr^{\beta}$, separates. The xanthene may also be obtained by passing a current of hydrogen chloride into an alcoholic solution of the xanthol. It forms white crystals, and melts at 164·5°. With iodine, it gives a compound rich in iodine, the crystals of which have a metallic lustre.

1 : 8-Dimethylxanthone can be obtained by distilling *p*-tolyl phosphate with potassium carbonate or from 6-p-*tolyloxy*-m-*toluic acid*, $C_6H_4Me\cdot O\cdot C_6H_3Me\cdot CO_2H$, which is produced by the action of sodium carbonate on *p*-tolyl carbonate. This acid melts at 113—114°. When the xanthone is treated as above, 1 : 8-*dimethylxanthene*,

$$C_6H_3Me<\underset{O}{\overset{CH_2}{}}>C_6H_3Me,$$

is formed. It is obtained in silvery-white scales which melt at 165°.

J. McC.

7-Hydroxy-2-phenyl-1 : 4-benzopyranol-4-carboxylic Acid and its Lactone. CARL BÜLOW and HERM. WAGNER (*Ber.*, 1903, 36, 1941—1953).—7-*Hydroxy*-2-*phenyl*-1 : 4-*benzopyranol*-4-*carboxylic acid*, $\begin{array}{l} \mathrm{OH\cdot C{=}CH\cdot C{-}{-}O{-}{-}CPh} \\ \mathrm{CH{:}CH\cdot C\cdot C(OH)(CO_2H)} \end{array}\!\!>\!CH$, is obtained in the form of its *hydrochloride*, $\begin{array}{l} \mathrm{OH\cdot CCl\cdot CH{:}C{-}O{-}CPh} \\ \mathrm{CH{:}CH\cdot C\cdot C(CO_2H)} \end{array}\!\!>\!CH$, when hydrogen chloride is led into a solution of resorcinol and benzoylpyruvic acid in acetic acid at a temperature of 60—80°. The hydrochloride forms an orange-red, crystalline powder only sparingly soluble in hot water, but readily so in boiling alcohol to which the theoretical amount of sodium acetate has been added, and also in most alkalis. The free acid is obtained when a concentrated solution of the hydrochloride in hot aqueous sodium acetate is mixed with acetic acid and allowed to cool; it crystallises in orange-coloured plates. The *picrate*, $C_{16}H_{10}O_4,C_6H_3O_7N_3$, forms orange-coloured crystals. When heated for some time with aqueous potassium hydroxide, the acid is decomposed yielding acetophenone and resorcinol, the latter being formed from the dihydroxybenzoylformic acid first produced. The latter has also been isolated in the form of lemon-yellow prisms, which, when dehydrated, melt at 194°.

When the acid is oxidised with an acetic acid solution of chromic anhydride, it yields Kostanecki's 7-hydroxy-2-phenyl-1 : 4-benzopyrone (3-hydroxyflavone) (Abstr., 1898, i, 369), and hence follows its constitution. When the carboxylic acid is acetylated either in pyridine solution or by boiling with acetic anhydride, sodium acetate, and acetic acid, it yields a *lactone*, $OAc\cdot C_9OH_4Ph<\substack{O\cdot CO \\ CO\cdot O}>C_9OH_4Ph\cdot OAc$, which crystallises in lemon-yellow plates melting at 157·5—158°. The corresponding *benzoyl* derivative melts and decomposes at 192°.

Resorcinol and ethyl benzoylpyruvate, under the conditions just described, yield *ethyl 7-hydroxy-2-phenyl-*1 : 4-*benzopyranol-*4-*carboxylate* in the form of its *hydrochloride.* The free ester is a brownish-violet, amorphous powder. The *picrate*, obtained by the union of one molecule of the quinonoid ester with one of picric acid, forms dark red crystals. When acetylated in pyridine solution, the ester yields a diacetyl derivative, namely, *ethyl 7-acetoxy-2-phenyl-*1 : 4-*acetylbenzopyranol-*4-*carboxylate* in the form of a syrup.

When the ester is boiled with acetic acid and sodium acetate, it yields the acetylated lactone melting at 157·5—158°. J. J. S.

Derivatives of α- and β-Naphthacoumarins. KURT BARTSCH (*Ber.*, 1903, 36, 1966—1976).—The author, by modifying von Pechmann's method of heating a mixture of α-naphthol, malic acid, and concentrated sulphuric acid, obtains a 25—30 per cent. yield of *α-naphthacoumarin*, $C_{13}H_8O_2$, which crystallises from alcohol in yellow needles and melts at 141—142°.

4-*Methyl-α-naphthacoumarin*, $C_{10}H_6<\substack{O\text{——}CO \\ CMe:CH}$, obtained by the condensation of α-naphthol and ethyl acetoacetate in concentrated sulphuric acid at 0°, crystallises in slender, snow-white, felted needles and melts at 167°.

3-*Ethyl-*4-*methyl-α-naphthacoumarin*, $C_{10}H_6<\substack{O\text{——}CO \\ CMe:CEt}$, prepared similarly from ethyl ethylacetoacetate, forms silvery leaflets and melts at 138°. *Ethyl-α-naphthacoumarin-*4-*carboxylate*, $C_{10}H_6<\substack{O\text{————}CO \\ C(CO_2Et):CH}$, obtained from α-naphthol and ethyl oxalate, separates from alcohol in pleochroic needles melting at 145—146°. Attempts to condense α-naphthol with ethyl benzoylacetate or ethyl acetonetricarboxylate by means of sulphuric acid were fruitless.

3-*Methyl-β-naphthacoumarin*, $C_{10}H_6<\substack{O\text{—}CO \\ CH:CMe}$, prepared by heating β-naphtholaldehyde with sodium propionate and propionic anhydride for 3 hours at 190—200°, crystallises from alcohol in slender needles and melts at 157—158°. 3-*Ethyl-β-naphthacoumarin*,

$$C_{10}H_6<\substack{O\text{—}CO \\ CH:CEt},$$

obtained similarly from β-naphtholaldehyde, sodium butyrate, and butyric anhydride, crystallises in long, yellow needles and melts at 110°. 3-*Phenyl-β-naphthacoumarin*, prepared from β-naphtholaldehyde,

sodium phenylacetate, and acetic anhydride, forms slightly yellow needles and melts at 142°.

The following substances were obtained by condensing β-naphtholaldehyde with dicarboxylic and ketonic acids. *Ethyl β-naphthacoumarin-3-carboxylate*, $C_{10}H_6<\begin{array}{l}O\text{—}CO\\ CH{:}C\cdot CO_2Et\end{array}$, obtained by boiling a mixture of the aldehyde with ethyl malonate and acetic anhydride, crystallises from alcohol in rosettes of yellow needles, melts at 115°, and on hydrolysis gives the *acid*, $C_{10}H_6<\begin{array}{l}O\text{—}CO\\ CH{:}C\cdot CO_2H\end{array}$, which crystallises in yellow needles melting at 234°.

Di-β-naphthacoumarin, $\begin{array}{l}O\text{——}CO\\ C_{10}H_6\cdot CH\end{array}\!\!>C\cdot C<\begin{array}{l}CO\text{—}O\\ CH\cdot C_{10}H_6\end{array}$, prepared by boiling the aldehyde with sodium succinate and acetic anhydride, crystallises from nitrobenzene in golden needles and melts above 300°.

3-β-Naphthacoumaryl methyl ketone, $C_{10}H_6<\begin{array}{l}O\text{—}CO\\ CH{:}C\cdot COMe\end{array}$, prepared from ethyl acetoacetate, crystallises from benzene in yellowish-green leaflets, melts at 187°, and gives a *phenylhydrazone*,

$$C_{10}H_6<\begin{array}{l}O\text{—}CO\\ CH{:}C\cdot CMe{:}N\cdot NHPh\end{array},$$

crystallising from acetone in long, red needles and melting and decomposing at 209—211°; the *dibromide*, $C_{15}H_{10}O_3Br_2$, prepared by heating the ketone with bromine for 6 hours at 100°, forms golden-yellow crystals and melts at 213°. *3-β-Naphthacoumaryl phenyl ketone*, $C_{10}H_6<\begin{array}{l}O\text{—}CO\\ CH{:}C\cdot COPh\end{array}$, prepared from ethyl benzoylacetate, crystallises from acetone in felted needles and melts at 207°.

2-Hydroxy-α-naphthylidene-α-naphthylamine, $OH\cdot C_{10}H_6\cdot CH{:}N\cdot C_{10}H_7$, obtained by the interaction of β-naphtholaldehyde with α-naphthylamine, forms red crystals and melts at 178°; the analogous β-naphthylamine *derivative* forms yellowish-red crystals and melts at 143°.

2-Ethoxy-1-naphthaldehyde, $OEt\cdot C_{10}H_6\cdot CHO$, obtained by ethylating β-naphtholaldehyde, crystallises from alcohol in long, slightly rose-coloured needles and melts at 109°. W. A. D.

Pasteur's Reaction. ZDENKO H. SKRAUP (*Monatsh.*, 1903, **24**, 291—309).—Oxidation with potassium or barium permanganate of β-*iso*-ψ-cinchonicine, prepared by heating β-*iso*cinchonine hydrogen sulphate at 140° (Abstr., 1900, i, 605), leads to the formation of cinchonic acid and β-*iso*meroquinenine. The "β-*iso*meroquinenine half" of the β-*iso*cinchonine molecule undergoes no change in the conversion of β-*iso*cinchonine into β-*iso*-ψ-cinchonicine.

The author discusses the bearing of the Pasteur reaction on the constitution of the cinchona alkaloids. G. Y.

Casimiroa Edulis. W. BICKERN (*Arch. Pharm.*, 1903, **241**, 166—176).—The seeds of this tree, which grows in Mexico and is known there as "zapote blanco," were found to contain about

0·63 per cent. of a crystalline glucoalkaloid, *casimirine*, $C_{30}H_{32}O_5N_2$. This melts at 106° and forms amorphous salts; when it is boiled with 30 per cent. hydrochloric acid, dextrose is eliminated gradually, and an *alkaloid* left containing about C, 73, H, 7 per cent. The hydrolysis may take place according to the equation $2C_{30}H_{32}O_5N_2 + H_2O = C_{54}H_{54}O_5N_4 + C_6H_{12}O_6$.

Accompanying the alkaloid, and less soluble than it in ether, is a substance $C_{27}H_{48}O_2$, melting at 207°, with the properties of a cholesterol or phytosterol; it is named *casimirol*. C. F. B.

Poisonous Principle contained in some kinds of Delphinium (Delphocurarine). GEORG HEYL (*Chem. Centr.*, 1903, i, 1187—1188; from *Südd. Apoth.-Zeit.*, 43, Nos. 28, 29, and 30).—An alkaloid, introduced into commerce under the name of delphocurarine (Merck) has been extracted from the roots of a number of *Delphiniums* by means of an 80 per cent. solution of alcohol containing tartaric acid. Delphocurarine consists in reality of a mixture of bases and behaves physiologically like curare (compare Lohmann, *Pflüger's Archiv*, 1902, **92**, 398). It forms a white, amorphous powder which has a very bitter taste and an alkaline reaction, and is readily soluble in dilute acids. A small quantity of a crystalline *compound*, $C_{23}H_{33}O_7N$, has been isolated from delphocurarine by means of ether and a mixture of ether and light petroleum; it crystallises in needles, melts at 184—185°, is rather readily soluble in alcohol, ether, chloroform, or benzene, but only sparingly so in light petroleum, and contains 18 per cent. of methoxyl. The platinum and gold salts form pale reddish-yellow powders, the former containing Pt 13·69 per cent., and the latter Au 23·29.

About 0·4 per cent. of a poisonous alkaloid has also been extracted from the bulbs of a *Zygadenus*. This compound melts at 134—135°, is readily soluble in ether, but almost insoluble in water, and forms a crystalline *hydrochloride* which is only slightly soluble in water. Potassium permanganate is an antidote for the delphinium alkaloids. E. W. W.

Preparation and Constitution of Histidine. SIGMUND FRÄNKEL (*Monatsh.*, 1903, **24**, 229—243).—Histidine, $C_6H_9O_2N_3$, discovered by Kossel as a decomposition product of sturine and obtained by Hedin from egg-albumin, has until now been classed with the diamino-acids, lysine and arginine, and obtained by precipitation with phosphotungstic acid. It is, however, soluble in excess of this acid, and the following simple method has been worked out for its preparation. Lawroff's observation (Abstr., 1901, i, 245), that by the hydrolysis of hæmoglobin 20 per cent of bases precipitated by phosphotungstic acid can be obtained, has been used as a starting point. Hæmoglobin was heated for 12 hours with fuming hydrochloric acid, the excess of acid removed by super-heated steam, the liquid concentrated, neutralised with sodium hydroxide, and made alkaline with sodium carbonate. Mercuric chloride dissolved in boiling alcohol was now added, and after several days the precipitate was separated, well washed, and decomposed with hydrogen sulphide.

The filtrate, on concentration to a syrup and shaking with ether, gave crystals of histidine hydrochloride. The ether also extracted small quantities of α-thiolactic acid, which was characterised by its colour reactions, and is thus proved to be among the decomposition products of hæmoglobin. The recrystallised histidine hydrochloride, $C_6H_9O_2N_3,HCl,H_2O$, melts at 80°, and loses the water of crystallisation at 140°. When shaken with excess of silver carbonate, free histidine, melting at 253°, was obtained in long, colourless crystals. Histidine does not contain methyl linked either to oxygen or nitrogen; it contains a carboxyl group, as it displaces carbon dioxide from silver and copper carbonates. Sodium hypobromite or nitrous acid displaces one nitrogen atom, which is also easily replaced by hydroxyl, and thus is present as an amino-group. These reactions lead to the partly developed formula, $NH_2\cdot C_5H_6N_2\cdot CO_2H$.

The complex $C_5H_6N_2$, *histine*, is not attacked when histidine is boiled with baryta; on dry distillation, the gases formed contain ammonia and give the pyrrole reaction. The pyrrole complex is, however, first formed on distillation, as histidine is not acted on by hydroxylamine. This proves that the remaining two nitrogen atoms of histidine are contained in a ring, and the observation that it gives a well-marked Weidel pyrimidine reaction with ammonia proves it to be an aminomethyldihydropyrimidinecarboxylic acid. Owing to the difficulty of oxidising histidine, the Weidel reaction is best carried out as applied by E. Fischer to xanthine, namely, the solution of histidine hydrochloride is warmed with a little potassium chlorate, evaporated to dryness, then hydrochloric acid containing a drop of nitric acid added, and again evaporated. Ammonia fumes now produce an intense red coloration which becomes reddish-violet on addition of sodium hydroxide. *Hydroxyhistinecarboxylic acid*, formed by the action of silver nitrite on histidine hydrochloride, crystallises in rosettes of long, colourless needles which melt and lose carbon dioxide at 204°. When heated at this temperature, a substance almost insoluble in boiling water and melting at 216° is formed; this is probably *hydroxyhistine*. Two formulæ thus remain possible for histidine:

$$\begin{array}{ccc} \begin{array}{l} NH\cdot CH_2\cdot C\cdot CH_2\cdot NH_2 \\ CH{:}N{-\!-}C\cdot CO_2H \end{array} & \qquad & \begin{array}{l} NH\cdot CH_2\cdot C\cdot NH_2 \\ CMe{:}N{-}C\cdot CO_2H \end{array} \\ \text{(i)} & & \text{(ii)} \end{array}$$

Of these, (i) is closely related to thymine, whereas (ii) shows the connection between histidine and the uric acid bases. E. F. A.

Syntheses in the Pyridine Series. VI. Hantzsch's Dihydropyridine Synthesis and its Extension. Emil Knoevenagel [with A. Erler & E. Reinecke] (*Ber.*, 1903, **36**, 2180—2190).—In many cases, 1 : 5-diketones do not react with alkylideneacetoacetic esters to form dihydropyridines; this has been explained by Rabe and Elze (Abstr., 1902, i, 709), who assume such diketones to be *cyclo*hexanol derivatives. In the present paper, evidence is adduced for the existence of open chain compounds, containing nitrogen, which cannot be

derived from *cyclo*hexanolones, and it is shown that these do not form dihydropyridines.

Ethyl acetylacetonemethylamine-benzylidene-acetoacetate, is obtained by heating its components together at the temperature of the water-bath, no trace of a pyridine derivative being formed; it forms white, crystalline plates melting at 198°. *Ethyl phenylaminocrotonate-benzylidene-acetoacetate*, the sole product obtained on heating its components together, forms asbestos-like crystals melting at 150°, which do not show fluorescence. On the other hand, benzylidenebenzoylacetone and benzoylacetoneamine yield a pyridine derivative, $C_{27}H_{23}O_2N$, which forms yellow crystals from alcohol melting at 222°. A similar compound, $C_{23}H_{23}O_3N$, produced when benzylidenebenzoylacetone is condensed with ethyl β-aminocrotonate, is yellow, crystalline, and melts at 174°.

Benzoylacetoneamine, $COPh·CH⁚CMe·NH_2$, formed by saturating the alcoholic solution of the ketone with ammonia, separates in colourless crystals melting at 143°. When condensed with ethylidene malonate, a molecule of alcohol is eliminated and a dihydropyridine derivative, $C_{17}H_{19}O_4N$, is obtained, which forms colourless crystals melting at 156°. Acetylacetoneamine and ethylidene malonate form a compound, $C_{14}H_{23}O_5N$, without elimination of alcohol; it forms white crystals melting at 75°. Attempts to close the pyridine ring by elimination of alcohol were not successful. E. F. A.

Compounds of Gold Chloride and Pyridine. Maurice François (*Compt. rend.*, 1903, **136**, 1557—1559).—Pyridine aurichloride, $C_5H_5N,HAuCl_4$, melts at 304°. By the action of water, this compound loses a mol. of hydrogen chloride, and yields the pale yellow substance, $C_5H_5N,AuCl_3$, which only crystallises with difficulty.

When an excess of anhydrous pyridine is added to auric chloride, an orange coloured substance is formed, and dissolves when the mixture is warmed. On cooling, small, orange-red crystals of the composition $(C_5NH_5)_2,AuCl_3$ are deposited. It is stable in air, but when heated at 100° loses a mol. of pyridine.

If an aqueous solution of auric chloride is boiled with pyridine, yellow, voluminous crystals are deposited on cooling, and these have the formula $(C_5H_5N)_2,AuCl_3,H_2O$. At 100°, this substance loses one mol. of pyridine and one mol. of water. J. McC.

Synthesis of Quinolines from Dinitriles. Reinhold von Walther (*J. pr. Chem.*, 1903, [ii], **67**, 504—512).—The action of diacetonitrile on an aqueous solution of sodium *o*-aminobenzoylformate, obtained by adding aqueous sodium hydroxide to isatine, leads to the formation of ammonia, water, and 3-*cyano*-2-*methylquinoline*-4-*carboxylic acid*, which crystallises in white leaflets or transparent plates, melts and decomposes at 238°, and is soluble in aqueous alkali hydroxides or in mineral acids. The *sodium* salt crystallises in matted, white needles, the *hydrochloride* crystallises in glistening, colourless, thick prisms, the *aurichloride* and *platinichloride* are partly decomposed by water. When heated with concentrated hydrochloric

acid at 250°, or when heated with soda-lime, it is decomposed with formation of quinaldine. It is hydrolysed by boiling concentrated aqueous sodium hydroxide with formation of 2-methylquinoline-3 : 4-dicarboxylic acid (Pfitzinger, Abstr., 1898, i, 207). 3-*Cyano-2-methylquinoline*, formed by the dry distillation of the carboxylic acid, crystallises in glistening, white prisms and melts at 125—127°. It forms a *hydrochloride*; a *platinichloride*, which crystallises in orange-red needles, becomes brown at 260°, but is not melted at 290°, and is decomposed by water; a *picrate*, which melts and decomposes at 208°; and a *chromate*, which crystallises in broad, yellow prisms. Solution of cyanomethylquinoline in boiling aqueous alkali hydroxides or dilute hydrochloric acid leads to the formation of a *substance* which crystallises in small, broad plates, melts and evolves gas at 190—200°, and resolidifies at 200°, and is soluble in alkalis or acids. Prolonged boiling of this substance or of the cyano-compound with concentrated aqueous alkali hydroxides leads to the formation of 2-methylquinoline-3-carboxylic acid, which yields quinaldine on dry distillation. If sodium carbonate or hydrogen carbonate is used in the formation of aminobenzoylformic acid from isatine, the action of diacetonitrile leads to the formation of cyanomethylquinolinecarboxylic acid and a *substance* which crystallises in white prisms, melts above 285°, and is insoluble in water, but soluble in acids or in boiling aqueous alkali hydroxides with evolution of ammonia. This substance is also formed by heating diacetonitrile with an aqueous solution of isatine, gives an odour of indole when heated with soda-lime, and is probably represented by the formula $NH{<}\substack{C_6H_4\\ CO—}{>}C{<}\substack{C(CN):CMe\\ C(CN):CMe}{>}NH$.

G. Y.

Acetonylnitromeconine. GILBERT BOOK (*Ber.*, 1903, 36, 2208—2215. Compare Abstr., 1902, i, 464).—*Acetonylnitromeconine-oxime*, $\begin{array}{l} OMe{\cdot}C — C(OMe){:}C{\cdot}CO{\cdot}O \\ \;\;\| \qquad\qquad\quad | \qquad\qquad\quad | \\ CH{\cdot}C(NO_2){:}C —— CH{\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH \end{array}$, crystallises from alcohol in small, yellow prisms melting at 170°; the *phenylhydrazone*, $C_{19}H_{19}O_6N_3$, forms felted, reddish-yellow needles melting at 184°, sparingly soluble in alcohol; and the *semicarbazone*, $C_{14}H_{16}O_7N_4$, crystallises from alcohol in small, yellow needles melting at 218°. 4 : 7-Dihydroxy-6-methoxydihydroquinaldine-5-carboxylic acid (*loc. cit.*) forms an aurichloride of unusual composition, $(C_{12}H_{13}O_5N)_2,HAuCl_4$, 2 mols. of the acid combining together to form an internal salt. The hydroxymethoxyquinaldine hydrochloride previously described melts at 232°, and the *picrate* at 233°. Under certain undetermined conditions, tin and hydrochloric acid reduce acetonylnitromeconine to 7-*hydroxy*-6-*methoxyquinaldine*-5-*carboxylic acid*, a reddish-grey compound melting at 212°, insoluble in water, alcohol, ether, or benzene. The *aurichloride*, $(C_{12}H_{11}O_4N)_2,HAuCl_4,H_2O$, melts at 168—170°. A product of further reduction is 4 : 7-*dihydroxy*-6-*methoxytetrahydroquinaldine*-5-*carboxylic acid*, the *hydrochloride* of which is precipitated from alcohol by ether in white, felted needles melting at 213°, and giving no phenol reaction with ferric chloride in aqueous solution. The *platinichloride* forms yellow needles which melt at 204°.

The reduction of acetonylnitromeconine also produces small quan-

tities of 7-*hydroxy*-6-*methoxydihydroquinaldine*-5-*aldehyde*, the *hydrochloride* of which melts at 226° and the *platinichloride* at 203°, and 7-*hydroxy*-6-*methoxy*-5-*hydroxymethyldihydroquinaldine*, melting at 226°, and forming an *aurichloride*, $C_{12}H_{15}O_3N,HAuCl_4,4H_2O$, which melts at 120—125°. C. H. D.

Naphthaphenoxazine Derivatives. OTTO FISCHER and EDUARD HEPP (*Ber.*, 1903, 36, 1807—1815).—Whilst indophenols are formed by the action of *p*-nitrosophenol on phenols, naphthoxazones are produced when β-naphthol is substituted for the phenol.

Naphthaphenoxazone, $O{:}C_6H_3{<}^{N}_{O}{>}C_{10}H_6$ $\left(\text{or } O{<}\begin{matrix}C_6H_3{:}N \\ | \qquad\quad | \\ O\text{——}C_{10}H_6\end{matrix}\right)$, prepared from *p*-nitrosophenol and β-naphthol in presence of anhydrous zinc chloride, crystallises from benzene in brown, flat needles, which soften at about 200° and melt completely at 211°. Its solution in sulphuric acid is of a deep bluish-green colour. When reduced by zinc dust and acetic acid, it forms a dihydro-compound, the diacetyl derivative of which was isolated as colourless needles melting at 206°.

Anilinonaphthaphenoxazone, prepared by boiling an alcoholic solution of the oxazone with a mixture of aniline and aniline hydrochloride, forms lustrous, green prisms and does not melt at 360°. The substitution of the anilino-group probably takes place in the position (10) para- to the bridge nitrogen atom.

2-*Hydroxynaphthaphenoxazone*,

$$\begin{matrix}CH{:}CH{\cdot}C{\cdot}N{:}C\text{————}C{\cdot}CH{:}CH \\ OH{\cdot}C{=}CH{\cdot}C{\cdot}O{\cdot}C{:}CH{\cdot}CO{\cdot}C{\cdot}CH{:}CH\end{matrix},$$

formed by the action of hydriodic acid on naphthaphenoxazone, crystallises in brownish-red prisms, the alkaline solution of which is strongly fluorescent. It is also formed from methyl iodide and naphthaphenoxazone together with its *methyl ether*, which crystallises from pyridine in reddish-brown needles melting at 270—271°.

Naphthaphenoxazoneoxime hydrochloride forms steel-blue prisms and readily suffers hydrolytic dissociation. The free base crystallises in dark green needles.

The behaviour of naphthaphenoxazone is in better harmony with the *p*-quinone than with the oxonium structure.

When the condensation of *p*-nitrosophenol and β-naphthol is carried out in the presence of concentrated hydrochloric acid, the yield of naphthaphenoxazone is small, the main product being *naphtholonaphthaphenoxazone*, $C_{26}H_{15}O_3N$. This results from the further action of the β-naphthol on the naphthaphenoxazone initially formed; it crystallises from a mixture of pyridine and alcohol in prisms with a bronze lustre and melts above 360°. When it is heated under pressure at 150—160° with a mixture of glacial acetic acid and concentrated hydrochloric acid, β-naphthol is one of the products. A. McK.

Thiocarbamides of the Phenylenediamines. GUSTAV FRERICHS and H. HUPKA (*Arch. Pharm.*, 1903, 241, 161—165).—When potassium thiocyanate is boiled with a phenylenediamine hydrochloride in molecular proportions in aqueous solution, a crystalline *aminophenyl-*

thiocarbamide, $NH_2·CS·NH·C_6H_4·NH_2$, is formed; the *para*-, *meta*-, and *ortho*-isomerides melt at 190°, 170°, and 167° respectively. All are monacid bases; their *hydrochlorides* and *hydrogen sulphates* were analysed. In the case of the *para*-isomeride, it was shown that ammonia was evolved on heating above the melting point with formation of *p*-phenylenethiocarbamide, $CS<\substack{NH\\NH}>C_6H_4$. Moreover, a little of this or of an isomeride was always formed alongside of the compounds already described. C. F. B.

Action of Amines on Derivatives of Trinitro-*p*-toluidine. AD. SOMMER (*J. pr. Chem.*, 1903, [ii], 67, 513—573. Compare Pinnow, Abstr., 1897, i, 338).—Trinitro-*p*-tolylmethylnitroamine is best prepared by nitration of Pinnow's mixture of two dinitrotolylmethylnitroamines (Abstr., 1901, i, 138).

By the action of amines on trinitrotolylmethylnitroamine, derivatives of the constitution
$C_6HMe(NO_2)_2(NMe·NO_2)X$ [$Me:(NO_2)_2:(NMeNO_2):X = 1:3:5:4:2$], are obtained.

3 : 5-*Dinitro-2-amino-4-methylnitroaminotoluene* crystallises in brownish-yellow, rectangular plates, melts at 178—178·5°, and is easily soluble in hot glacial acetic acid or acetone, but insoluble in light petroleum. 3 : 5-*Dinitro-4-methylnitroamino-2-anilinotoluene*, obtained along with diazoaminobenzene (Laubenheimer, *Ber.*, 1875, 9, 768, 1828) by the action of aniline, crystallises in light brown cubes, melts at 134°, and is easily soluble in ethyl acetate. 3 : 5-*Dinitro-4-methylnitroamino-2-*p*-toluidinotoluene* crystallises in dark orange-red needles and melts at 184°. Derivatives could not be obtained by the action of *o*-toluidine, methylaniline, α-naphthylamine, or tribromoaniline. 3 : 5-*Dinitro-4-methylnitramino-2-β-naphthylaminotoluene* crystallises in golden leaflets and melts at 131°. 3 : 5-*Dinitro-4-methylnitroamino-2-*p*-chloroanilinotoluene*, obtained together with 4 : 4′-dichlorodiazoaminobenzene, crystallises in yellow needles and melts at 193°.

3 : 5-*Dinitro-4-methylnitroamino-2-dimethylaminotoluene* [$X = NMe_2$], obtained by the action of dimethylamine, crystallises in bronze needles and melts at 126—127°. The action of methylamine leads to the formation of dinitrodimethyltolylenediamine.

5-*Nitro-3-nitroso-4-methylnitrosoaminotoluene-2-azobenzene*,

$$NO·C_6HMe(NO_2)(NMeNO)·N_2Ph,$$

formed by the action of phenylhydrazine on trinitrotolylmethylnitroamine or on trinitrotolylmethylnitrosoamine (compare Willgerodt and Ferko, Abstr., 1888, 829), crystallises in light yellow, silky needles, melts and decomposes violently at 174°, is moderately soluble in benzene, less so in alcohol or acetone, and neutral to acids or bases, and gives Liebermann's nitroso-reaction.

3 : 5-*Dinitro-2-amino-4-methylaminotoluene*,

$$NH_2·C_6HMe(NO_2)_2·NHMe,$$

is formed by the action of alcoholic ammonia on trinitromethyltoluidine at 100°, or of phenol on dinitromethylnitroaminotoluidine at 140—160°. It crystallises in clusters of orange-coloured needles and melts at 206—208°. 3 : 5-*Dinitro-2-anilino-4-methylaminotoluene* crys-

tallises in thick prisms and melts at 197°. 3 : 5-*Dinitro-2-toluidino-4-methylaminotoluene* crystallises in blood-red needles and melts at 164°. The action of phenylhydrazine on trinitromethyltoluidine leads to the formation of 3 : 5-*dinitro-4-methylaminotoluene-2-hydrazobenzene*, $NHMe \cdot C_6HMe(NO_2)_2 \cdot N_2H_2Ph$, which forms matted, red, hair-like crystals and melts at 155°. These dinitrotolylenediamines are weak bases.

That these bases are *meta-* and not *ortho*-diamines is proved by the failure of attempts to obtain an iminoazole derivative by the action of acetic anhydride, acetic anhydride and sulphuric acid, acetamide, or aminoacetic acid on dinitromethyltolylenediamine, and by the formation of 3 : 5-dinitro-4-methylnitroaminotoluene (Romburgh, *Rec. trav. chim.*, 1884, 3, 1404) on removal by diazotisation of the amino-group of dinitromethylnitroaminotoluidine.

Treatment of the mixture of two dinitrotolylmethylnitroamines with ammonia leads to the formation of 3-*nitro-4-methylnitroamino*-o-*toluidine* from the γ-nitroamine. It forms impure crystals and is soluble in sulphuric acid. The β-nitroamine, which remains unchanged, melts at 122°, and on treatment with phenol and sulphuric acid in amyl alcoholic solution yields Pinnow's β-dinitromethyl-*p*-toluidine (Abstr., 1901, i, 138). When boiled with aqueous potassium hydroxide, trinitromethyltoluidine yields methylamine, nitrous acid, and an impure phenol (compare Hepp, Abstr., 1883, 315). 3 : 5-*Dinitrotolylenedimethyldiamine*, $C_6HMe(NO_2)_2(NHMe)_2$, formed by the action of methylamine on trinitromethyltoluidine, is obtained in two modifications. The *red* modification crystallises in leaflets, melts at 169—170°, and on recrystallisation from acetone is converted into the *yellow* form, which crystallises in needles, melts at 110°, and changes into the red modification at 140°. The action of aqueous potassium hydroxide on either modification leads to the formation of Kostanecki's 3 : 5-dinitro-2 : 4-dihydroxytoluene (Abstr., 1888, 264) and of 3 : 5-*dinitro-2-methylamino*-p-*cresol*, which crystallises in long, yellow needles and melts at 177° (compare Laubenheimer, *loc. cit.*).

When boiled with aqueous potassium hydroxide, dinitromethyltolylenediamine yields 3 : 5-*dinitro-2-amino*-p-*cresol*, which crystallises in brownish-red needles, sinters at 135°, and melts at 141—142°. It forms an insoluble *sodium* and a yellow *ammonium* derivative. With alcoholic ammonia, it forms a dark green, iridescent *substance*, probably a dinitrotolylenediamine. Prolonged boiling of dinitromethyltolylenediamine with aqueous potassium hydroxide leads to the formation of dinitrohydroxytoluene.

Trinitro-*o*-cresol (Nölting and Collin, Abstr., 1884, 1012) is converted by boiling aqueous potassium hydroxide into dinitrodihydroxytoluene melting at 90°. The action of alcoholic methylamine on trinitro-*o*-cresol leads to the formation of *methylamine dinitromethylamino-3-tolyloxide*, which crystallises in golden needles, decomposes at 208°, and on addition of sulphuric acid yields 3 : 5-*dinitro-4-methylamino*-o-*cresol*, crystallising in red needles and melting at 151°. The *silver* derivative is formed by the action of silver nitrate on the methylamine derivative as a blood-red precipitate. The *methyl ether* crystallises in yellow needles and melts at 117·5°. The *ethyl ether* contains alcohol

of crystallisation, melts at 95°, solidifies, and melts again at about 160°. When heated with ammonia at 100°, the ethyl ether forms dinitromethyltolylenediamine melting at 206—208°.

The following nitroso-derivatives have been prepared from the secondary amines. 3 : 5-*Dinitro*-2 : 4-*dinitrosomethylaminotoluene* crystallises in glistening cubes or silvery leaflets and melts at 132°. 3 : 5-*Dinitro*-2-*methylamino*-4-*nitrosomethylaminotoluene*, prepared by the action of methylamine on trinitrotolylmethylnitrosamine (Pinnow, Abstr., 1897, i, 338), crystallises in yellowish needles and melts at 186—187°. 3 : 5-*Dinitro*-4-*nitrosomethyl*-o-*toluidine* crystallises in brownish-yellow prisms and melts at 164°. 3 : 5-*Dinitro*-2-*nitrosoanilino*-4-*nitrosomethylaminotoluene* crystallises in clusters of yellow needles and decomposes at about 100°. 3 : 5-*Dinitro*-2-*anilino*-4-*nitrosomethylaminotoluene* forms orange-coloured needles and melts at 122°. 3 : 5-*Dinitro*-2-*nitrosoanilino*-4-*methylnitroaminotoluene* crystallises in yellowish-white needles and melts at 141°. When treated with nitric and nitrous acids, trinitromethyltoluidine and dinitrodimethyltolylenediamine yield their nitrosoamines. Dinitrodimethyltolylenediamine is charred by sulphuric and nitrous acids; the dinitrosoamine, on treatment with alcohol and dilute sulphuric acid, yields a mixture of dinitronitrosomethyltoluidine and dinitromethyltoluidine (compare Gattermann, Abstr., 1885, 975).

The action of dimethylamine on trinitromethyl-*p*-toluidine leads to the formation of 3 : 5-*dinitro*-2-*dimethylamino*-4-*methylaminotoluene*, which crystallises in yellow needles, melts at 115°, and is reduced by alcoholic ammonia and hydrogen sulphide to 5-*nitro*-2-*dimethylamino*-4-*methylamino*-m-*toluidine*; this crystallises in prisms and melts at 61·5—62°. The action of acetic anhydride on the triaminotoluene leads to the formation of 7-*nitro*-4-*dimethylamino*-1 : 2 : 5-*trimethylbenziminoazole*, which crystallises in yellow leaflets and melts at 146·5°. G. Y.

Pyrimidine Derivatives. Alfred Byk (*Ber.*, 1903, 36, 1915—1926. Compare Gabriel, Abstr., 1899, i, 638; 1900, i, 53; 1901, i, 168, 427; 1902, i, 59, 498).—Guanidine carbonate readily condenses with a hot alcoholic solution of ethyl acetoacetate, yielding 2-*amino*-6-*hydroxy*-4-*methyl*-5-*ethylpyrimidine*,

$$NH_2\cdot C{<}{\genfrac{}{}{0pt}{}{N{-}CMe}{N{:}C(OH)}}{>}CEt,$$

which crystallises from hot water in large, rhombic prisms terminated by pyramids; it decomposes about 285°, and dissolves readily in alcohol and acetic acid and also in dilute alkalis and acids. When heated with concentrated hydrochloric acid at 180° for 24 hours, it is converted into 2 : 6-*dihydroxy*-4-*methyl*-5-*ethylpyrimidine*, which crystallises in long needles, decomposes and melts at 236—238°, and dissolves in alkalis and also in concentrated hydrochloric acid.

2 : 6-*Dichloro*-4-*methyl*-5-*ethylpyrimidine*, obtained by the action of phosphorus oxychloride on the dihydroxy-compound, crystallises from water in small, colourless needles, melts at 39°, distils at 255°, and is readily soluble in most organic solvents, but does not dissolve in alkalis and dilute mineral acids. When reduced with zinc dust and

water, it yields 4-*methyl-5-ethylpyrimidine*, which is best isolated in the form of its sparingly soluble *mercurichloride*, $C_7H_{10}N_2,2HgCl_2$; this crystallises in small needles, and decomposes and melts at 155°. The free base, $C_7H_{10}N_2$, is a colourless oil distilling at 193·5° under 758 mm. pressure, has an odour resembling that of quinoline, and dissolves in water, but gives no precipitate with potassium dichromate, silver nitrate, or potassium ferrocyanide. The *hydrochloride* crystallises in minute needles and is volatile at 100°, the *platinic chloride* derivative, $(C_7H_{10}N_2)_2PtCl_4$, melts between 210° and 214°, and the *gold chloride* derivative, $C_7H_{10}N_2,AuCl_3$, melts at 104—106°.

6-*Chloro-2-amino-4-methyl-5-ethylpyrimidine* crystallises in small, felted needles, melts at 156°, and is fairly readily soluble in most organic solvents and in hydrochloric acid. The *picrate* melts at 192—193°. 2-*Amino-4-methyl-5-ethylpyrimidine*, obtained by the reduction of the chloro-derivative, melts at 168—169°, distils at 250° under 764 mm. pressure, and is sparingly soluble in ether or acetone. The *hydrochloride* crystallises in plates. With platinic chloride, it yields golden-red needles, and with auric chloride short prisms.

2 : 6-*Diamino-4-methyl-5-ethylpyrimidine*, obtained by the action of alcoholic ammonia on the monochloro-compound at 140°, crystallises in octahedra, melts at 161—162°, distils at about 310°, and has strongly basic properties. The *hydrochloride* crystallises in quadratic prisms, the *platinichloride*, $C_7H_{12}N_4,H_2PtCl_6$, crystallises in yellow, hexagonal plates, and changes colour at about 220°.

2-*Amino-6-anilino-4-methyl-5-ethylpyrimidine* crystallises from alcohol in prisms, melts at 158—159°, and can be distilled.

2-*Amino-6-thio-4-methyl-5-ethylpyrimidine*, $C_7H_{11}N_3S$, obtained by the action of potassium hydrosulphide in alcoholic solution on the monochloro-compound at 100°, crystallises in small, yellow prisms, and changes colour at about 210°. It dissolves in alcohols, acids, and alkalis, but is only sparingly soluble in ether, chloroform, benzene, or light petroleum.

2-*Chloro-6-amino-4-methyl-5-ethylpyrimidine*, obtained by the action of alcoholic ammonia on the dichloro-compound at 100°, crystallises in small needles and melts at 222°. Aniline converts the dichloro-derivative into 2 : 6-*dianilino-4-methyl-5-ethylpyrimidine*, which has been isolated in the form of its *hydrochloride*, $C_{19}H_{20}N_4,HCl$. This changes colour at 285°, is completely decomposed at 297°, and is only sparingly soluble.

2 : 6-*Dithio-4-methyl-5-ethylpyrimidine*, $C_7H_{10}N_2S_2$, crystallises in yellow needles, changes colour at 250°, and is completely molten at 280°.

4-Methylpyrimidine (Gabriel, Abstr., 1899, i, 638) is reduced by sodium and ethyl alcohol to $\alpha\gamma$-diaminobutane (Tafel, Abstr., 1901, i, 72). J. J. S.

Derivatives of 2 : 4 : 6-Trichloropyrimidine. Ernst Büttner (*Ber.*, 1903, 36, 2227—2235).—Gabriel (Abstr., 1902, i, 59) has shown that 2 : 4 : 6-trichloropyrimidine is converted into the triamino-derivative by the action of alcoholic ammonia above 200°. The author

proves that at the ordinary temperature 2 : 4 : 6-trichloropyrimidine reacts with alcoholic ammonia to form a mixture of 2 : 4-*chloro*-6-*aminopyrimidine* and 4 : 6-*chloro-2-aminopyrimidine*, which are easily separated owing to the sparing solubility of the former in benzene. 2 : 4-Chloro-6-aminopyrimidine melts at 271° ; 4 : 6-chloro-2-aminopyrimidine melts at 221° and is easily volatile with steam. Both compounds form stellate crystals on sublimation. The constitution of 4 : 6-chloro-2-aminopyrimidine was determined by its formation from malonylguanidine and phosphorus oxychloride ; further, when reduced by zinc dust, it yields 2-*aminopyrimidine*, melting at 127—128° and forming a *hydrochloride* melting at 196°, a *platinichloride* melting and decomposing at 216°, and a *picrate* melting at 237—238°. When 4 : 6-chloro-2-aminopyrimidine is heated in a sealed tube with a mixture of fuming hydriodic acid and phosphonium iodide at 100°, 4-*hydroxy*-6-*iodo*-2-*aminopyrimidine* is produced ; from its alkaline solution, it is precipitated in tiny, white needles, which give off iodine vapour at 241°.

2 : 4-Chloro-6-aminopyrimidine is not reduced by water and zinc dust but, when heated with fuming hydriodic acid and phosphonium iodide, it is converted into 4-*iodo*-6-*aminopyrimidine*, which forms white needles, melts at 211° to a blood-red liquid, and at a slightly higher temperature decomposes with evolution of iodine vapour. When heated with alcoholic ammonia in a sealed tube at 180—200°, it is acted on with difficulty to form a diaminopyrimidine melting at about 267°. When 4-iodo-6-aminopyrimidine is boiled with zinc dust and water, it forms 6-*aminopyrimidine* melting at 150—152°.

4-*Chloro*-2 : 6-*aminopyrimidine* is produced by heating 2 : 4 : 6-trichloropyrimidine with alcoholic ammonia at 160°, and forms rhombic plates melting at 198°. When heated with hydriodic acid and red phosphorus until hydrogen chloride ceases to be evolved, it is converted into 4-*iodo*-2 : 6-*aminopyrimidine*, which forms colourless crystals melting at 187—188°, and is reducible by zinc dust and water to 2 : 6-*diaminopyrimidine*. The latter compound, which may also be directly prepared from 4-chloro-2 : 6-aminopyrimidine by reduction with zinc dust and fuming hydrochloric acid, melts at 144—145° and forms a *platinichloride* which does not melt at 270°.

2 : 4 : 6-*Trithiopyrimidine* is prepared by the addition of 2 : 4 : 6-trichloropyrimidine to an alcoholic solution of potassium hydrosulphide. By the action of sodium methoxide on trichloropyrimidine in the cold, a *dichloromethoxypyrimidine* crystallising in needles and melting at 51° was formed ; further methylation of this compound gives a *chlorodimethoxypyrimidine* melting at 73°. When 2 : 4 : 6-trichloropyrimidine is heated with sodium methoxide in a sealed tube at 100°, 2 : 4 : 6-*trimethoxypyrimidine* is formed ; it crystallises in needles melting at 53°. A. McK.

Pyrazole Series. III. Antipyrine. LUDWIG KNORR (*Annalen*, 1903, **328**, 62—87).—I. *Behaviour of Nitrosoantipyrine towards Hydrazines*.—[With FRITZ MÜLLER.]—Nitrosoantipyrine and phenylhydrazine (Knorr and Geuther) yield an additive product which

crystallises well and melts at 210°. It has the formula $C_{17}H_{19}O_2N_5$ and closely resembles a similar *additive* product, $C_{17}H_{18}O_2N_5Br$, which is formed from *p*-bromophenylhydrazine and nitrosoantipyrine and crystallises in colourless leaflets, or with one mol. of ethyl acetate, in prisms, melting and decomposing at 205°. A comparison with Bamberger's azohydroxyamides shows that these substances do not belong to this type of compounds. When boiled with sodium hydroxide, the additive compound of phenylhydrazine and nitrosoantipyrine yields *s*-phenylmethylhydrazine and phenylmethyl*iso*nitrosopyrazolone (m. p. 156°); similarly, the product formed frcm *p*-bromophenylhydrazine yields *s*-phenylmethylhydrazine and p-*bromophenylmethyl*iso*nitrosopyrazolone*, which crystallises in orange-yellow prisms melting at 188°.

The phenylhydrazone of *iso*nitrosoacetoacetanilide decomposes into *iso*nitrosophenylmethylpyrazolone under the influence of alkalis; accordingly, the additive product of phenylhydrazine and nitrosoantipyrine must be the phenylhydrazone of *iso*nitrosoacetoacetophenylmethylhydrazide, NHPh·N:CMe·C(:NOH)·CO·NPh·NHMe, formed by cleavage of the pyrazolone ring of antipyrine.

When hydrazine was used instead of phenylhydrazine, the intermediate hydrazone was not isolated, but *iso*nitroso-3-methylpyrazolone (m. p. 230°), $\begin{matrix} NH\cdot CO \\ | \quad\quad \\ N{=}CMe \end{matrix}\!\!>\!C{:}N\cdot OH$, and *s*-phenylmethylhydrazine were formed directly.

II. *Constitution of Antipyrine.*—Since the interaction of phenylhydrazine and nitrosoantipyrine and the action of sodium hydroxide and carbon dioxide on antipyrine both lead to the formation of compounds belonging to the acid amide type, it is concluded that antipyrine contains the linking –N·CO–, and that there is no justification for the phenolbetaine formula recently suggested by Michaelis (Abstr., 1902, i, 315). The action of phosphorus oxychloride on antipyrine, deduced by Michaelis in support of his views, which leads to the formation of the methochloride of 5-chloro-1-phenyl-3-methylpyrazole, which can again be reconverted into antipyrine by alkalis, can be equally easily interpreted by means of the author's formula if the intermediate production of the hydrochloride of antipyrine be assumed.

K. J. P. O.

Action of Phenylhydrazine on Benzylidenebisacetoacetic Ester. EMIL KNOEVENAGEL and F. HEEREN (*Ber.*, 1903, **36**, 2124—2129).—*Ethyl benzylidenebisacetoacetate phenylhydrazone*, $C_{25}H_{30}O_5N_2$, forms colourless, silky needles melting at 193°. It thus differs from the phenylhydrazone, described by Rabe and Elze (*loc. cit.*), melting at 168—171°.

Phenylhydrazine reacts with ethyl 3-phenyl-1-methyl*cyclo*hexene-5-one-2:4-dicarboxylate to form a reddish-yellow, crystalline compound, $C_{23}H_{24}O_4N_2$, melting at 171°. When heated with potassium hydroxide, this forms an *acid*, $C_{21}H_{18}O_3N_2$, which crystallises in colourless prisms melting at 180°. When heated at 190° for several hours, this loses carbon dioxide, and a substance $C_{20}H_{18}ON_2$ is formed, which melts at 217—218°.

Attempts were made to synthesise this compound. Phenylbenzylidenemethylpyrazolone, when condensed with ethyl acetoacetate in presence either of sodium ethoxide or diethylamine, formed an additive compound melting at 160°, which was also formed by the condensation of phenylmethylpyrazolone and ethyl benzylideneacetoacetate. All attempts to convert this into a *cyclo*hexenone derivative failed.

Phenylbenzylidenemethylpyrazolone condenses with deoxybenzoin in a similar manner to form an additive compound, $C_{31}H_{26}O_2N_2$, which crystallises from alcohol in colourless crystals melting at 201°. When exposed to the air, this gradually takes up a molecule of water and then melts at 195°. E. F. A.

New Synthesis of α-Phenylbenziminoazole. Bronislas Pawlewski (*Bull. Acad. Sci. Cracow*, 1903, 4, 227—228).—2-Phenylbenziminoazole, $CPh{<}^{NH}_{N}{>}C_6H_4$, prepared by heating *o*-phenylenediamine and thiobenzamide in a sealed tube at 240—250°, crystallises in needles melting at 290—292° (Hübner, Hinsberg, and Koller give 280°). A. McK.

Synthesis of Triazoles by the Action of Sodium on Nitriles. Reinhold von Walther and E. Krumbiegel (*J. pr. Chem.*, 1903, [ii], 67, 481—503. Compare this vol., i, 582, and Engelhardt, Abstr., 1897, i, 126).—Ammonia was evolved, but no crystallised triazole could be obtained, by the action of sodium on benzonitrile and *o*-tolylhydrazine, *o*-toluonitrile and *o*-tolylhydrazine, and *o*-toluonitrile and *p*-tolylhydrazine. The following triazoles have been obtained by the action of sodium on the nitrile and hydrazine. In some cases, the amide corresponding with the nitrile and the hydrocarbon corresponding with the hydrazine are formed, the yield of the triazole being diminished. 1-o-*Tolyl*-3 : 5-*di*-p-*tolyltriazole*, formed from *p*-toluonitrile and *o*-tolylhydrazine, crystallises in yellow needles and melts at 137°. 3 : 5-*Diphenyl*-1-p-*tolyltriazole*, formed along with benzamide and toluene from benzonitrile and *p*-tolylhydrazine, crystallises in thick needles, melts at 108—109°, and is easily oxidised by chromic acid in acetic acid solution. 1 : 3 : 5-*Tri*-p-*tolyltriazole*, from *p*-toluonitrile and *p*-tolylhydrazine, forms prismatic crystals and melts at 134°. 3 : 5-*Diphenyl*-1-m-*xylyltriazole*, formed together with *m*-xylene and benzamide from benzonitrile and *as.*-*m*-xylylhydrazine, separates from alcohol in yellow crystals and melts at 85°. 3 : 5-*Di*-p-*tolyl*-1-m-*xylyltriazole*, formed, together with *p*-toluamide and *m*-xylene, from *as.*-*m*-xylylhydrazine and *p*-toluonitrile, crystallises in white needles and melts at 159°. 1-o-*Chlorophenyl*-3 : 5-*diphenyltriazole*, formed together with benzamide and chlorobenzene from benzonitrile and *o*-chlorophenylhydrazine, crystallises in needles and melts at 108°.

1-o-*Chlorophenyl*-3 : 5-*di*-p-*tolyltriazole*, from chlorophenylhydrazine and toluonitrile, melts at 159°. 1-m-*Chlorophenyl*-3 : 5-*diphenyltriazole*, formed together with benzamide from *m*-chlorophenylhydrazine and benzonitrile, melts at 107—109°. 1-m-*Chlorophenyl*-3 : 5-*di*-p-*tolyltriazole*, formed with *p*-toluamide from *m*-chlorophenylhydrazine and

p-toluonitrile, separates in prismatic crystals and melts at 121°. 1-p-*Chlorophenyl*-3 : 5-*diphenyltriazole*, from *p*-chlorophenylhydrazine and benzonitrile, forms yellow, crystalline aggregates and melts at 119°. 1-p-*Chlorophenyl*-3 : 5-*di*-p-*tolyltriazole* crystallises in delicate, yellow needles and melts at 155°.

Tri-p-*chlorophenyltriazole*, which is formed in small amount together with *p*-chlorobenzamide and chlorobenzene from *p*-chlorophenylhydrazine and *p*-chlorobenzonitrile, crystallises in needles and melts at 168—170°.

1-p-*Bromophenyl*-3 : 5-*di*-p-*tolyltriazole*, from *p*-bromophenylhydrazine and *p*-toluonitrile, crystallises from alcohol and melts at 168°.

1-p-*Chloro*-o-*tolyl*-3 : 5-*diphenyltriazole*, which crystallises in yellow matted needles and melts at 103—104°, and 1-p-*chloro*-o-*tolyl*-3 : 5-*di*-p-*tolyltriazole*, which forms a yellow, crystalline powder and melts at 170°, are obtained from *p*-chloro-*o*-tolylhydrazine.

m-Chlorobenzamide and chlorobenzene, but not a triazole, are obtained by the action of sodium on *m*-chlorophenylhydrazine and *m*-chlorobenzonitrile. No action was observed with sodium, *p*-nitrophenylhydrazine, and benzonitrile. G. Y.

Preparation of Benzotriazoles. KARL ELBS and W. KEIPER (*J. pr. Chem.*, 1903, [ii], 67, 580—584. Compare Kehrmann and Messinger, Abstr., 1892, 889).—Derivatives of *o*-nitrobenzeneazobenzene are reduced to the corresponding benzotriazoles (ψ-aziminobenzenes) by zinc dust in warm alkaline solution, or electrolytically with a nickel gauze cathode in dilute alkaline solution.

2-p-*Hydroxyphenylbenzotriazole*, $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}N\cdot C_6H_4\cdot OH$, obtained from *o*-nitrobenzeneazophenol, crystallises in delicate, grey needles, melts at 217—219°, and is only slightly soluble in water, easily so in warm organic solvents or in aqueous sodium hydroxide, but insoluble in sodium carbonate solution or in acids.

o-*Nitrobenzeneazosalicylic acid*, prepared by coupling diazotised *o*-nitroaniline with salicylic acid, forms a brownish-red, crystalline powder, melts at 215—217°, and is slightly soluble in water, but easily so in warm alcohol or glacial acetic acid. The alkali salts dissolve easily in water to dark red solutions. *Benzotriazole*-2-*salicylic acid*, $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}N\cdot C_6H_3(OH)\cdot CO_2H$, obtained on reduction, crystallises in delicate, white needles, melts at 296—297°, and is almost insoluble in water, but moderately so in organic solvents. The *sodium* salt is only slightly soluble.

4-*Hydroxynaphthyl*-2-*benzotriazole*, obtained on reduction of *o*-nitrobenzeneazo-α-naphthol, crystallises in red, microscopic needles, melts at 203—204°, and is soluble in dilute aqueous sodium hydroxide. The ethereal solution has a slight blue fluorescence. G. Y.

Electrolytic Preparation of Azobenzene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 141535).—An alkaline suspension of nitrobenzene is reduced electrolytically to azobenzene

(D.R.-P. 127727). If a higher temperature (105—115°) and concentrated sodium hydroxide solution are employed, the product is azoxybenzene, containing only small quantities of aniline and hydrazobenzene. The iron vessel is made the cathode, the anode being a small, rapidly rotating iron stirrer. C. H. D.

β-Naphthol-6-azo-2-nitrophenol-4-sulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 141538).—The diazonium compound of 2-chloro-3-nitroaniline-5-sulphonic acid (compare this vol., i, 665) combines with β-naphthol to form a red dye, which exchanges its chlorine atom for a hydroxyl group when boiled with sodium hydroxide, forming β-naphthol-6-azo-2-nitrophenol-4-sulphonic acid, identical with the dye prepared from 2-nitro-6-aminophenol-4-sulphonic acid.
C. H. D.

Benzoyl Derivatives of Hydrazobenzene. PAUL FREUNDLER (*Compt. rend.*, 1903, **136**, 1553—1556).—Benzoylhydrazobenzene, NHPh·NPhBz, is best obtained by the benzoylation of hydrazobenzene in pyridine solution with the requisite quantity of benzoyl chloride. It exists in two forms; from alcohol, acetone, or acetic acid, it separates in crystals which melt at 138—139° (compare Biehringer and Busch, this vol., i, 296), but from chloroform, benzene, or light petroleum it crystallises in tabular prisms which melt at 126°. If the second modification be heated for some time at 90°, it changes into the form melting at 138°.

If excess of benzoyl chloride is used in the benzoylation, a mixture of mono- and di-benzoylhydrazobenzenes is formed. When benzoylhydrazobenzene is benzoylated in anhydrous pyridine solution with benzoyl chloride, *dibenzoylhydrazobenzene*, NPhBz·NPhBz, is formed; it crystallises from hot acetone in small, thick prisms, melts at 161—162°, and is sparingly soluble in the common solvents.

By treating hydrazobenzene with benzoyl chloride in presence of a 10 per cent. solution of sodium hydroxide, dibenzoylhydrazobenzene was obtained (m. p. 161°), and not benzanilide as stated by Biehringer and Busch (*loc. cit.*). By the pyridine process, *benzoyl-o-hydrazotoluene* has also been prepared; it melts at 123·5—124° and is soluble in cold alcohol.

A mixture of benzoyl chloride and pyridine can be used for benzoylation, and the solution keeps well so long as it is protected from moisture. This suggests that pyridine chlorobenzoate, $C_5NH_5Cl\cdot COPh$, is formed, and the mechanism of the reaction is to be explained by the intermediary production of this substance (Einhorn and Hollandt, Abstr., 1898, i, 577). The author does not agree with Wedekind's criticism (Abstr., 1901, i, 499). J. McC.

Diazoniumazides, Az·N_5. ARTHUR HANTZSCH (*Ber.*, 1903, **36**, 2056—2058).—*p-Nitrobenzenediazoniumazide*, $NO_2\cdot C_6H_4\cdot\underset{\underset{N}{||}}{N}\cdot N<\genfrac{}{}{0pt}{}{N}{\underset{N}{||}}$, is formed as a white precipitate on mixing nitrobenzene*anti*diazo-

hydroxide and ethyl azoimidecarboxylate, and explodes when dry with a brilliant, white flash of light.

p-*Benzoylbenzenediazoniumazide*, $C_6H_5\cdot CO\cdot C_6H_4\cdot N_2\cdot N_3$, is more stable than the preceding compound, and explodes at 116—117°.

Tribromophenylnitrosoamine, $C_6H_2Br_3\cdot NH\cdot NO$, does not react in this way, but the diazonium nitrate yields tribromobenzeneazoimide, $C_6H_2Br_3\cdot N_3$. T. M. L.

Diazonium Fluorides. ARTHUR HANTZSCH and R. VOCK (*Ber.*, 1903, 36, 2059—2061).—*Benzenediazonium acid fluoride* can be prepared by diazotising a solution of aniline in a mixture of acetic and hydrofluoric acids at low temperatures by means of amyl nitrite; on adding ether, the fluoride separates either in white flocks or as a yellow oil, which solidifies when rubbed and can be purified by repeated washing with ether. The p-*bromo*-derivative behaves in a similar manner and gives *p*-bromophenol when boiled with water or decomposed with moist copper powder. The *tribromo*-derivative, $C_6H_2Br_3\cdot N_2F,HF,2H_2O$, is much more stable, remains constant in weight for some time at the ordinary temperature, and could therefore be analysed. The p-*nitro*-derivative, $NO_2\cdot C_6H_4\cdot N_2F,2HF,H_2O$, was also analysed; at the ordinary temperature, it soon becomes yellow and then brown owing to formation of aminoazo-compounds; on heating with water, it gives *p*-nitrophenol; with alcohol, nitrobenzene; with copper chloride, *p*-chloronitrobenzene; and with moist copper-powder, *p*-nitrophenol, but no fluorobenzene derivatives. T. M. L.

Interaction of Diazonium Salts and Alcohols. ARTHUR HANTZSCH and R. VOCK (*Ber.*, 1903, 36, 2061—2064. Compare Abstr., 1902, i, 62).—Phenol ethers appear to be the normal product of interaction of diazonium salts with alcohols, hydrocarbons being formed in increasing proportion as the molecular weight of the alcohol and the acid character of the phenyl radicle increase. With benzenediazonium chloride, *n*- and *iso*-propyl alcohols interact in the same way as methyl and ethyl alcohols, giving phenyl propyl ethers and no trace of propaldehyde or acetone; amyl alcohol gives both phenyl amyl ether and valeraldehyde, or its condensation products, and benzyl alcohol gives benzaldehyde with only a little phenyl benzyl ether. Glycerol behaves like propyl alcohol, giving the monophenyl ether and a little resin, and mannitol and benzoin are not attacked. Tribromobenzenediazonium sulphate, however, oxidises all the univalent alcohols to aldehydes or ketones, but instead of smoothly oxidising glycerol to glycerose, and mannitol to mannose, gives only resins and tribromobenzene.

Monobromophenyl glycerol ether, $C_6H_4Br\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, crystallises from dilute alcohol and melts at 81°. T. M. L.

Reduction of Diazo-compounds. ARTHUR HANTZSCH and R. VOCK (*Ber.*, 1903, 36, 2065—2069).—All normal diazo-oxides are reduced by alkaline stannous solutions to phenylhydrazine and benzene, whilst the *anti*diazoxides are not attacked; the single

exception is tribromobenzeneantidiazoxide, which, when heated, is reduced to tribromobenzene.

It is suggested that the substance actually reduced is not the diazoxide or its ion, but the undissociated diazonium hydroxide or its hydroxide:

$$\begin{array}{c}Ar{\cdot}N\\ \| \\ NaO{\cdot}N\end{array} \rightleftarrows \begin{array}{c}Ar{\cdot}N\\ \| \\ HO{\cdot}N\end{array} \rightleftarrows \begin{array}{c}Ar{\cdot}N{\cdot}OH\\ | \\ HO{\cdot}N{\cdot}H\end{array} \rightleftarrows \begin{array}{c}Ar{\cdot}N{\cdot}OH\\ \| \\ N\end{array},$$

and that the reduction takes place through an additive compound of the diazonium hydroxide and phenylhydrazine:

$$\begin{array}{c}Ph\\ HO\end{array}\!\!>N{:}N + \begin{array}{c}H\\ |\\ N_2H_2Ph\end{array} \longrightarrow \begin{array}{cc}Ph & H\\ | & |\\ N & \!\!-\!\!N\\ | & |\\ HO & N_2H_2Ph\end{array} \longrightarrow \begin{array}{c}C_6H_6\\ N_2\\ HOH + N_2 + C_6H_6\end{array}.$$

T. M. L.

Migration of Atoms in Diazo-compounds. ARTHUR HANTZSCH (*Ber.*, 1903, 36, 2069—2075).—The isomeric change observed in the case of *o*- and *p*-dibromo- and tribromo-diazonium chlorides does not take place in the tri-iodo-chloride nor in the tribromo-fluoride, and is not therefore conditioned merely by the different atomic weight of the halogens.

Tri-iodoaniline is best prepared by mixing solutions in concentrated hydrochloric acid of aniline and of iodine chloride. *Tri-iododiazonium chloride* differs from the aniline hydrochloride in that it has a neutral reaction and is stable towards water; it is only moderately explosive, and detonates at 120° when heated in a melting point tube, and also occasionally when merely spread on porous earthenware.

In reply to the criticisms of Orton (this vol., i, 297), it is stated that tribromophenylnitrosoamine is undoubtedly formed below 0°, and if the operation is carried out carefully the amount of dibromodiazophenol is so small that it remains entirely in solution, leaving a pure solid nitrosoamine. The nitrosoamine is readily converted above 0° into dibromodiazophenol, and is almost certainly a usual intermediate product of change. T. M. L.

2-Nitro-6-diazophenol-4-sulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 141750).—*2-Chloro-3-nitroaniline-5-sulphonic acid*, prepared by reduction of dinitrochlorobenzenesulphonic acid with ferrous hydroxide (D.R.-P. 116759), forms a yellow, crystalline potassium salt, which explodes when heated. The diazonium compound forms yellow leaflets, and on treatment with sodium carbonate exchanges its chlorine atom for a hydroxyl group, yielding a diazo-acid identical with that obtained by the action of nitrous acid on 2-nitro-6-aminophenol-4-sulphonic acid. C. H. D.

Action of Iodine Bromide on Proteids and Organic Bases. ANTOINE MOUNEYRAT (*Compt. rend.*, 1903, 136, 1470—1472).—When iodine bromide, dissolved in alcohol, is added to an aqueous solution of a peptone, an albumose, pyridine, quinoline, morphine, codeine, strychnine, brucine, narceine, quinine, or hexamethyleneamine, yellow to brown

precipitates of additive products are formed, corresponding with the iodine chloride addition products obtained by Dittmar (Abstr., 1886, 158). With amides and xanthine bases, no precipitates are formed.

The *pyridine* compound, C_5H_5N,BrI, forms yellow needles, melts at 115—117°, furnishes a *hydrobromide*, and is converted by ammonia into the black, explosive *substance*, C_5H_5N,INH_2. The *quinoline additive product* melts at 138—140°.

Dittmar's view (*loc. cit.*) that these substances are only formed with pyridine derivatives is regarded by the author as untenable since hexamethyleneamine furnishes a product of this type. T. A. H.

Proteids. II. Friedrich Kutscher (*Zeit. physiol. Chem.*, 1903, 38, 111—134. Compare Kossel and Kutscher, Abstr., 1901, i, 107). —Tables are given of the amounts of ammonia, histidine, arginine, lysine, tyrosine, and glutamic acid obtained from such different proteids as gluten-casein, glutin-fibrin, gliadin, mucedin, zein, and thymus-histon. Full details of the methods employed are given. For the determination of the glutamic acid, use was made of the *zinc* salt, $C_5H_7O_4NZn,2H_2O$, which crystallises in glistening prisms or small needles, is sparingly soluble (0·064 in 100 parts of water at 100°), and is completely dehydrated at 150°.

Zinc aspartate is readily soluble in water and has not been obtained in a crystalline condition.

The silver derivatives of histidine, thymin, uracil, and cytosine are stable even in the presence of an excess of barium hydroxide, whereas the silver salts of the amino-acids are readily decomposed by barium hydroxide.

From the results obtained, it appears probable that gliadin and mucedin are identical. J. J. S.

Formation of Guanidine by Oxidation of Gelatin with Permanganates. Friedrich Kutscher and Goswin Zickgraf (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 28, 624—629).—It was claimed by Béchamp (*J. Pharm. Chim.*, [iii], 31, 32) that carbamide is a product of the oxidation of proteids by potassium permanganate, but Lossen has shown (Abstr., 1880, 413) that this is incorrect, since guanidine, and not carbamide, is formed. As Pommerrening (Abstr., 1902, ii, 274) has questioned Lossen's results, the authors have conclusively established them by obtaining guanidine by the oxidation of gelatin with barium or calcium permanganate.

Guanidine is formed by the oxidation of arginine, which is, accordingly, a guanidine derivative. Since guanidine can be obtained by the direct oxidation of proteids, it must be derived from that grouping in the proteid molecule which yields arginine on being hydrolysed, a conclusion which could not be maintained if Pommerrening's contention were correct.

Gelatin was chosen in place of egg-albumin or casein, since it yields arginine more readily than either of the latter proteids. To its solution in boiling water, a solution of calcium permanganate was gradually added. Guanidine was readily formed, and was identified by

conversion into its picrate. Other products of the oxidation were hydrogen cyanide, butyric acid, carbon dioxide, and ammonia.

When a proteid is hydrolysed, the protamine ring (Kossel) yields histidine, arginine, and lysine, whilst the side chains give leucine, tyrosine, &c., on the one hand, and cystine, alanine, and glutamic acid on the other. When a proteid is oxidised, the products are such as one would expect from the oxidation of the preceding products of hydrolysis, namely, hydrogen cyanide derived from histidine; guanidine and succinic acid from arginine; hydrogen cyanide, glutamic acid, and glutaric acid from lysine; butyric acid from leucine. A. McK.

Anti-albumid and the Anti-group in the Proteid Molecule. TH. ROTARSKI (*Zeit. physiol. Chem.*, 1903, 38, 552—554).—The existence of hemi- and anti-groups in the proteid molecule is denied. The substance, named anti-albumid by Kühne, can only be obtained in small quantities, and if the proteid has not been coagulated before digestion, none is obtainable. Like the so-called anti-peptone, it is a mixture of substances, and is obtained only if the proteid has been "denaturalised." W. D. H.

Chlorophyll, Hæmoglobin, and Lipochrome. LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1903, 38, 196—197).—Methylethylmaleic anhydride has been condensed with hydrocarbons in the presence of aluminium chloride according to Pechmann's method (Abstr., 1882, 1074), and the action of dehydrating agents on the condensation products, which show great similarity to the lipochromes, is being studied. J. J. S.

Cytosine. ALBRECHT KOSSEL and H. STEUDEL (*Zeit. physiol. Chem.*, 1903, 38, 49—59. Compare this vol., i, 303, and 451).—Details are given for the preparation of cytosine from the testicles of the sturgeon. Cytosine may also be obtained by heating yeast nuclein with dilute sulphuric acid for 2 hours at 150°. The base yields a *nitrate*, $C_4H_5ON_3,HNO_3$, a *basic sulphate*, $(C_4H_5ON_3)_4,H_2SO_4$, which crystallises in small needles sparingly soluble in water, and an *acid sulphate*, $C_4H_5ON_3,H_2SO_4$, which may be obtained from the mother liquors of the basic sulphate. Nitrous acid transforms cytosine into uracil, although the yield is not good, and barium permanganate oxidises it to oxalic acid and biuret. These reactions are in harmony with the view that cytosine is 6-*amino-2-oxypyrimidine*, $NH_2{\cdot}C{\lessdot}\genfrac{}{}{0pt}{}{N\text{—}CO}{CH{:}CH}{\gtrdot}NH$, although the products formed on oxidation are also in harmony with the formulæ $NH_2{\cdot}C{\lessdot}\genfrac{}{}{0pt}{}{NH{\cdot}CO}{C{=}CH}{\gtrdot}NH$ and $NH_2{\cdot}C{\lessdot}\genfrac{}{}{0pt}{}{NH{\cdot}CO}{CH{\cdot}CH}{\gtrdot}N$. The relationship between the constitutional formulæ of cytosine (6-amino-2-oxypyrimidine) and uric acid is very close, and the transformation of the former into the latter can be theoretically accomplished by a process of oxidation and addition of cyanic acid. It is suggested that these reactions probably occur in the animal system. J. J. S.

Preparation of Cytosine. FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1903, 38, 170—177).—Thymus-nucleic acid is hydrolysed with 33 per cent. sulphuric acid under pressure and the products precipitated with phosphotungstic acid (compare Kossel and Neumann, Abstr., 1894, i, 631). The precipitate is decomposed by baryta, and the liquid obtained acidified with nitric acid and precipitated with concentrated silver nitrate solution. The filtrate from this is again precipitated with silver nitrate until it gives a brown precipitate with barium hydroxide. The second silver precipitate is decomposed by hydrogen sulphide, and cytosine crystallises from the filtrate after the silver sulphide has been removed. A base has also been obtained from the nucleic acid of yeast, which in many respects resembles cytosine. From an analysis of the picrate, it appears to contain an amino-group in place of one of the hydrogen atoms of cytosine, and is probably a diamino-oxypyrimidine.

Cytosine forms a well-defined additive compound with silver nitrate.

J. J. S.

Preparation and Analyses of Nucleic Acids. III. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1903, 38, 80—83).—In addition to thymine and cytosine, uracil is also produced when the nucleic acid of the spleen is hydrolysed with 25 per cent. sulphuric acid. Details of the separation are described. Cytosine sulphate is given the formula $(C_4H_5ON_3)_2,H_2SO_4$, whereas Kossel and Steudel (this vol., i, 667) describe only a basic and an acid sulphate. J. J. S.

Enzymatic Decomposition of Nucleic Acids. TRASABURO ARAKI (*Zeit. physiol. Chem.*, 1903, 38, 84—97. Compare Hahn and Geret, Abstr., 1901, i, 59; Kutscher, *ibid.*, ii, 466 and 523; 1902, ii, 153).—The "Kernsubstanz" from the red corpuscles of birds' blood is readily rendered soluble by trypsin, and less readily by an enzyme which is contained in thymus extract.

Trypsin decomposes *a*-thymus-nucleic acid (Neumann, Abstr., 1899, i, 467; 1900, i, 319), yielding as an intermediate product the *b*-acid, which can then be further decomposed by prolonged tryptic digestion. Thymus extract behaves in exactly the same manner, as do also Cohnheim's erepsin (Abstr., 1902, ii, 413) extract of liver and of spleen.

J. J. S.

Nucleic Acid. PHOEBUS A. LEVENE (*Proc. Amer. physiol. Soc.*, 1903, xvii; *Amer. J. Physiol.*, 9).—Improved methods for obtaining the pyrimidine bases enable silver to be dispensed with in the preparation of thymine and cytosine. On decomposition of the nucleic acids of the spleen and pancreas, three bases, thymine, cytosine, and uracil, were found. The nucleic acid of yeast yielded, on hydrolysis, only the two last named. W. D. H.

Gorgonin and Iodogorgonic Acid. MARTIN HENZE (*Zeit. physiol. Chem.*, 1903, 38, 60—79. Compare Drechsel, Abstr., 1896, ii, 378; Mendel, *Amer. J. Physiol.*, 4, 243).—The following product are obtained when gorgonin is hydrolysed with dilute sulphuric acid

namely, arginine and lysine in appreciable amounts, histidine in small quantity, tyrosine and leucine together with considerable amounts of free iodine, hydrogen sulphide, and ammonia. Phenylalanine and iodogorgonic acid are also probably formed, but glycine, cystine, aspartic and glutamic acids are not produced. When the hydrolysis is effected by the aid of baryta water, the products are iodogorgonic acid, lysine, tyrosine, and glycine.

Iodogorgonic acid is sparingly soluble in water, and forms long, pointed crystals which melt and decompose at 205°. It dissolves readily in alkalis and forms salts with mineral acids. The hydrochloride is not decomposed by water. Analyses ($N = 3{\cdot}78$, and $I = 57{\cdot}32$) prove that the acid cannot be an iodoaminobutyric acid ($N = 6{\cdot}11$, and $I = 55{\cdot}46$). J. J. S.

Suprarenin (Adrenalin). OTTO VON FÜRTH (*Monatsh.*, 1903, **24**, 261—290. Compare Abstr., 1900, ii, 292; 1902, i, 68).—The action of hydrogen sulphide on the iron derivative of suprarenin suspended in water, and addition of ammonia to the concentrated filtrate, leads to the formation of crystalline suprarenin, which is identified with adrenalin. Aldrich's formula, $C_9H_{13}O_3N$, for suprarenin is probably correct.

The action of concentrated mineral acids on suprarenin leads to the formation of methylamine and of a *substance*, ($C_{35}H_{25}O_{11}N_3$?), which is obtained as a violet powder. It dissolves in acids to yellowish-brown, in alkalis to carmine, solutions, is insoluble in alcohol, ether, acetone, or chloroform, reduces ammoniacal silver solutions, but not Fehling's solution. In slightly acid solution, it gives precipitates with phosphotungstic acid, mercury potassium iodide, potassium periodide, picric acid, and the salts of the heavy metals.

When heated with water at 220°, suprarenin yields a product which closely resembles Abel's epinephrin.

With benzenesulphonic chloride, suprarenin yields a *tribenzenesulpho*-derivative, $C_9H_{10}O_3N(SO_2Ph)_3$, which is insoluble in water, soluble in organic solvents, and, when acted on by nitric acid, yields a *substance*, $C_9H_7NO_5(SO_2Ph)_2$.

The *tribenzoyl* derivative of suprarenin forms a hard, granular mass, and is soluble in alcohol, chloroform, acetone, or pyridine, but is insoluble in light petroleum.

The action of methyl iodide on suprarenin leads to the formation of an amorphous *substance*, which gives no precipitate with silver nitrate except on addition of a drop of nitric acid or of ammonia, evolves iodine at 120° in a vacuum, and at higher temperatures yields a *substance* which gives the pyrrole reaction.

Moderate oxidation of suprarenin with hydrogen peroxide in presence of ferric salts or with potassium or barium permanganate leads to the formation of an acid substance which is easily soluble in water, reduces ammoniacal silver solutions, yields a volatile base when boiled with alkalis, and forms pyrrole when fused with alkalis.

When fused with potassium hydroxide at 200°, suprarenin yields protocatechuic acid.

The author represents the present state of knowledge as to the groupings in the suprarenin molecule by the partially developed formula $[(CH_3)NC_2H(OH)]C_6H_6(OH)_2$. G. Y.

Epinephrin. John J. Abel (*Ber.*, 1903, 36, 1839—1847. Compare Abstr., 1899, i, 395).—Adrenalin, first obtained by Takamine by the action of ammonia on concentrated suprarenal extract, is obtained pure, either by precipitation with ammoniacal zinc chloride and removal of the zinc with hydrogen sulphide, or by adding a solution of trichloroacetic acid to the finely-divided gland, concentration of the filtrate under reduced pressure, and addition of ammonia to this. It is well to extract the pulped suprarenal gland two or three times with the acid. The purified, colourless prisms have the composition $C_{10}H_{13}O_3N,\frac{1}{2}H_2O$. On benzoylation, epinephrin benzoate, $C_{17}H_{15}O_4N$, was obtained, which on hydrolysis gave the alkaloid form of epinephrin now shown to have the composition $C_{10}H_{13}NO_3$. The conversion of adrenalin into the alkaloid form is best brought about by dissolving it in strong sulphuric acid, and after 24 hours pouring the solution into alcohol. The sulphate, $(C_{10}H_{13}O_3N)_2,H_2SO_4$, is a greyish-white powder, easily soluble in water. E. F. A.

Reducing Enzymes. M. Emm. Pozzi-Escot (*Amer. Chem. J.*, 1903, 29, 517—563. Compare Abstr., 1902, i, 513, 580, 654, 655; ii, 577, 635).—The essential characteristic of de Rey-Pailhade's philothion is its property of forming hydrogen sulphide from free sulphur. The preparation of an active hydrogenising liquid containing philothion by plasmolysing yeast cells is described.

The action of oxygen on philothion is discussed; philothion does not act as an oxydase, but it may cause oxidation as a secondary reaction to reduction. When, under suitable conditions, an excess of a reductase acts on an oxydase, the latter becomes paralysed in its action. By the action of oxygen alone, philothion is slowly oxidised; by the action of oxydase alone, philothion is not destroyed; by the action of oxydase in presence of oxygen, philothion is oxidised in a few hours (de Rey-Pailhade). Potatoes contain both oxydases and reductases, and in presence of oxygen the oxidising action preponderates, the reducing action being destroyed. All parts of the potato tuber seem to be equally rich in oxydases, but do not possess the same oxidising property, since a state of equilibrium may be established between the oxydases and reductases. In a solution containing a mixture of the two enzymes, the oxydases are more readily precipitated by absolute alcohol than are the reductases.

When a solution containing philothion is agitated with flowers of sulphur, the formation of hydrogen sulphide takes place in the cold. The presence of alkalis renders philothion much more sensitive to the action of oxygen. Reductases cannot be detected by a colour reaction with guaiacum tincture. Experiments are described to show that potassium nitrate in dilute solution is reduced to nitrite by philothion; it was also shown that reduction takes place where cells rich in reductases are employed, instead of extracting the philothion to begin with. In accordance with the experiments of Abelous and Gérard (Abstr., 1900, ii, 226), it is proved by the author that nitrobenzene can be reduced to aniline by philothion. Sulphates can also be reduced by secretions related to philothion. The action of philothion on hydrogen peroxide has also been studied; the volume of oxygen liberated by the same amount of enzyme with increase of time was

measured, and it is considered most probable that the enzyme does not act as a catalyser; the optimum temperature for the preceding decomposition was 30—40°. The most active paralysers were those salts with an acid reaction. The property of decomposing hydrogen peroxide to the extent shown by philothion, is equalled by one other definite enzyme only, namely, Loew's catalase. The behaviour of philothion and catalase is very similar, although Loew describes catalase as an oxydase; the author considers them to be identical. When fibrin is extracted from blood, it carries with it the greater part of the reductases. The oxidising properties of the reductases and their physiological *rôle* are discussed. A. McK.

The Function of Peroxides in the Living Cell. VI. Catalases. Alexis Bach and Robert Chodat (*Ber.*, 1903, 36, 1756—1761. Compare Abstr., 1902, ii, 344, 522; this vol., i, 377, 378).—On account of the rapid and complete decomposition of hydrogen peroxide by catalases with evolution of inert oxygen, Loew (Abstr., 1902, ii, 522) has denied the physiological importance of hydrogen peroxide. In the living cell, however, organic peroxides are also formed and rendered active by peroxydases, and the behaviour of catalases towards these compounds has not been studied. Catalase was prepared from a pure culture of *Sterigmatocystis nigra*, a fungus whose resisting power towards hydrogen peroxide is about four times as great as that of *Penicillium glaucum*, and was purified from reducing substances. It is entirely without action on ethyl hydroperoxide or on oxygenase, which is to be regarded as a mono-substituted hydrogen peroxide. Further, catalase has no influence on the action of peroxydase in rendering active hydrogen peroxide or oxygenase. The catalase is not destroyed by the peroxydase, but is found to be undiminished in activity at the end of the reaction. Catalase, therefore, only decomposes that portion of the hydrogen peroxide which is not used for oxidising purposes by the peroxydase.

Pozzi-Escot (Abstr., 1902, i, 513) has assumed the identity of catalase with reductase or philothion, which is also said to decompose hydrogen peroxide with evolution of inert oxygen. It is shown, however, that pure catalase has no reducing action on sulphur, and is therefore distinct from reductase. C. H. D.

Action of Phosphorus Pentachloride on Anthranilic Acid. Emil Uhlfelder (*Ber.*, 1903, 36, 1824—1828).—By the action of phosphorus pentachloride on *m*-aminobenzoic acid, Michaelis (this vol., i, 390) obtained the *N*-oxychlorophosphine, $COCl\cdot C_6H_4\cdot NH\cdot POCl_2$, together with the anhydride, $NH_2\cdot C_6H_4\cdot CO\cdot O\cdot CO\cdot C_6H_4\cdot NH_2$. *p*-Aminobenzoic acid was also found by Michaelis to behave in an analogous manner, but no definite products were isolated when anthranilic acid was used.

The N-*oxychlorophosphine*, $COCl\cdot C_6H_4\cdot NH\cdot POCl_2$, obtained from phosphorus pentachloride and anthranilic acid, crystallises from light petroleum in large, colourless prisms melting at 62°. Whilst the corresponding phosphines of the meta- and para-series react with methyl

alcohol to form *N*-phosphinates (Michaelis, *loc. cit.*), this phosphine forms the hydrochloride of methyl anthranilate, from which the ester was isolated and further identified by conversion into its benzoyl derivative.

Phenyl N-*phosphino-o-aminobenzoate*, $CO_2Ph \cdot C_6H_4 \cdot NH \cdot PO(OPh)_2$, formed from phenol and the preceding *N*-oxychlorophosphine, separates from absolute alcohol in white, rhombic crystals melting at 94°. When heated with water, it behaves similarly to the meta- and para-compounds, anthranilic acid being formed.

A substance of the composition $COCl \cdot C_6H_4 \cdot N[PO(NH \cdot C_6H_4 \cdot COCl)_2]_2$ is formed as a by-product from the action of phosphorus pentachloride on anthranilic acid. It is sparingly soluble in ether, and can thus be separated from the readily soluble *N*-oxychlorophosphine. It crystallises in yellow needles melting at 148—153°; when boiled with methyl alcohol, it forms methyl anthranilate and *methyl-*N-*phosphino-di-o-aminobenzoate*, $PO_2Me(NH \cdot C_6H_4 \cdot CO_2Me)_2$, which separates in needles and melts at 174°. A. McK.

A New Organic Base containing Phosphorus. Its Constitution, and some of its Salts. Paul Lemoult (*Compt. rend.*, 1903, 136, 1666—1668).—The compound obtained by Gilpin (Abstr., 1897, i, 463) by the action of phosphorus pentachloride on aniline is the *hydrochloride* of *trianilinophenylphosphimide*, $P(NHPh)_3\colon NPh$. This hydrochloride can be recrystallised from hot alcohol. When a warm alcoholic solution of the hydrochloride is treated with potassium hydroxide, decomposition occurs, and after removal of the potassium chloride, trianilinophenylphosphimide separates from the solution in slender, white needles which melt at 232° and are insoluble in water. The *sulphate* can be obtained from a solution of the base or of the hydrochloride and melts at 312—313°; if excess of sulphuric acid be used in the preparation, the *hydrogen sulphate* is obtained in small, white crystals. The *nitrate* crystallises well in long needles and melts at 240°. The *platinichloride* separates in yellow crystals. J. McC.

Organic Chemistry.

Dibromoacetylene; Purification, Cryoscopy, Analysis. Paul Lemoult (*Compt. rend.*, 1903, 137, 55—56. Compare this vol., i, 595).—Pure dibromoacetylene is prepared by distilling a mixture of tribromoethylene and alcoholic potassium hydroxide in a current of nitrogen, and collecting the heavy drops which distil at 76—77° under boiled-out water.

The molecular weight found by depression of the freezing point of acetic acid was 183·3, whilst CBr:CBr requires 184. A Carius estimation of the bromine gave 87·57 per cent. of Br, whilst C_2Br_2 requires 86·95. It is therefore proved that dibromoacetylene can be obtained pure when fractionated as soon as it is formed. J. McC.

Preparation of Primary Alcohols by means of the Corresponding Acids. Louis Bouveault and Gustave Blanc (*Compt. rend.*, 1903, 137, 60—62. Compare this vol., i, 597).—The reduction previously described (*loc. cit.*) can also be applied to the lower acids. With these, however, the experimental difficulties are greater. Amyl acetate, when reduced in amyl alcohol solution with sodium, gives ethyl alcohol.

Methyl butyrate in ethyl alcoholic solution with sodium gives *n*-butyl alcohol, which is separated with difficulty from the ethyl alcohol. Its presence is identified by the formation of its phenylurethane.

Methyl decoate is easily reduced by this method, and gives a good yield of *n*-decyl alcohol, which boils at 120° under 12 mm. pressure.

Methyl myristate is also easily reduced, but the separation of the reduction product from the sodium myristate, which is simultaneously formed, is difficult. The alcohol formed is *n*-tetradecyl alcohol; it melts at 38° and boils at 160° under 10 mm. pressure.

Ethyl benzoate, or other aromatic ester with the carboxyl group directly linked to the benzene nucleus, is not reduced. On the other hand, ethyl phenylacetate gives a good yield of phenylethyl alcohol, the phenylurethane of which melts at 80°.

Ethyl hexahydrobenzoate, on reduction with sodium, gives *hexahydrobenzyl alcohol* as a viscid oil with characteristic odour which boils at 82° under 11 mm. pressure. Its *phenylurethane* forms acicular crystals, melts at 82°, is soluble in the common organic solvents, but is insoluble in light petroleum. J. McC.

Removal of Water from Secondary Alcohols of High Molecular Weight. Hermann Thoms and C. Mannich (*Ber.*, 1903, 36, 2544—2550).—Methyl nonyl ketone condenses with aminoguanidine to form a *compound* which separates in minute, fatty scales, and melts at 79°; its *picrate* melts at 148—149°. The *aminoguanidine*-derivative of methyl heptyl ketone melts at 66—67° and its picrate at 154°.

Good yields of methylnonylcarbinol and methylheptylcarbinol can be obtained by reducing the ketones with sodium and alcohol. Methyl-

nonylcarbinol is a viscous liquid, boils at 120° under 14 mm. pressure, has sp. gr. 0·8263 at 18°, and when boiled with 60 per cent. sulphuric acid yields the ether, $O(CHMe{\cdot}C_9H_{19})_2$, and Δ^{β}-undecylene, $CH_3{\cdot}CH{:}CH{\cdot}C_8H_{17}$, which is oxidised by potassium permanganate to pelargonic acid; about 4 per cent. of Δ^{α}-undecylene, $CH_2{:}CH{\cdot}C_9H_{19}$, is also produced; the hydrocarbons could not be separated directly, but were converted into dibromides, and these by alcoholic potash into hydrocarbons of the acetylene series; the undecinene (nonylacetylene), $CH{:}C{\cdot}C_9H_{19}$, was separated with alcoholic silver nitrate (compare this vol., i, 678).

Methylheptylcarbinol, $C_7H_{15}{\cdot}CHMe{\cdot}OH$, boils at 193—194° under atmospheric pressure, and at 87·5° under 10 mm. pressure; it gives a nonylene boiling at 147—148°, which is oxidised to heptoic acid.

T. M. L.

Chlorohydrin and Oxide of αδ-Dihydroxypentane. BRUNO POSSANNER VON EHRENTHAL (*Monatsh.*, 1903, **24**, 351—356).—Acetylpropyl alcohol, prepared by the interaction of sodium ethoxide, ethyl acetoacetate, and ethylene dibromide under conditions unsuitable for the formation of ethyl diacetyladipate (compare Lipp, Abstr., 1889, 843), was reduced by sodium amalgam to αδ-dihydroxypentane (compare Perkin and Freer, Trans., 1887, **51**, 836). *αδ-Dihydroxypentanechlorohydrin*, formed by heating αδ-dihydroxypentane at 100° with excess of hydrochloric acid, is a clear liquid, which boils at 70—80° under 12 mm. pressure. The oxide, prepared by heating it with powdered potassium hydroxide, boils at 77—79°, and is not reconverted into the glycol when heated with water for 6 hours at 120—130°. The oxide, when prepared in this manner, is identical with that obtained by heating the glycol either with water or with 60 per cent. sulphuric acid (compare Froebe and Hochstetter, this vol., i, 320).

A. McK.

Esterification of the Hydracids. ANTOINE VILLIERS (*Compt. rend.*, 1903, **137**, 53—55. Compare this vol., i, 598, 599).—The velocity of esterification of hydrochloric acid is so slow at the ordinary temperature that solutions prepared 25 years ago seem not yet to have attained the limit; furthermore the results obtained by direct esterification are very different from those obtained by decomposition of the hydrochloric ester. Ordinary ether is produced with hydrochloric acid only at high temperatures.

For the monatomic alcohols the velocity of esterification with hydrochloric acid decreases as the molecular weight of the alcohol rises: it is noticeable, however, that the velocity for amyl alcohol is greater than for *iso*propyl alcohol. Butyl alcohol is esterified exceptionally slowly, and the limit is probably less at the ordinary temperature than at 100°.

The esterification of glycol and glycerol with hydrochloric acid is much more rapid than that of ethyl alcohol. The limit attained is probably less than that reached at 100°, but is the same as that at 44°, and this suggests a difference in the mode of action of the hydrochloric acid hydrates on glycol and glycerol from that on ethyl alcohol.

J. McC.

Fatty Acids of Egg-lecithin. H. Cousin (*Compt. rend.*, 1903, **137**, 68—70).—The acids were obtained from lecithin by saponifying with alcoholic potassium hydroxide and then acidifying with hydrochloric acid. They were formerly supposed to be oleic, stearic, and palmitic, but the iodine value of the unsaturated acid was found to be higher than that corresponding with oleic acid. The mixture, therefore, contains an acid which is less saturated than oleic acid.

A quantity of the mixed acids was transformed into the barium salts, and the mixed salts were treated with a mixture of benzene and alcohol; the acid regenerated from the dissolved part was proved to be linoleic acid, because when oxidised in alkaline solution with permanganate it gave tetrahydroxystearic acid, melting at 171—172°.

The undissolved residue was converted into lead salt, and this was treated with ether. From the ethereal solution oleic acid was obtained. From the lead salt insoluble in ether a mixture of stearic and palmitic acids was obtained. The quantity of stearic acid varied from 30 to 40 per cent., and that of palmitic acid from 60 to 70 per cent., in different specimens.

No other acids than these mentioned could be found in the egg-lecithin. J. McC.

A Possible Method of preparing Organic Sulphur Compounds. Alwin Mittasch (*J. pr. Chem.*, 1903, [ii], **68**, 103—104). —When a current of hydrogen or coal gas is passed through carbon disulphide and then through a moderately heated combustion tube filled with nickel powder, an organic sulphur compound, which is either a mercaptan or a thio-ether, is formed. It forms a derivative with mercuric oxide, which melts at 65—70°. G. Y.

Organo-mineral Anhydrides. Amé Pictet (*Arch. Sci. phys. nat.*, 1903, [iv], **15**, 589—611).—By the direct union of nitric, phosphoric, pyrophosphoric, arsenious, sulphuric, chromic, or boric acid with various organic acids, mixed anhydrides are formed. Of these, the anhydride of nitric and acetic acids is described.

[With Paul Genequand.]—A cryoscopic determination of the molecular weight of *diacetylorthonitric acid* (Abstr., 1902, i, 584) in ethylene dibromide and in bromoform shows that it has the formula $C_4H_9O_7N$. A vapour density determination by Meyer's method, using xylene (138°) in the outer bath, shows that the compound is completely dissociated about 10° above its boiling point. By the action of varying quantities of acetic acid on nitric acid, it was proved that the greatest development of heat takes place when molecular quantities are mixed, and no compound other than $N(OAc)_2(OH)_3$ is produced.

With E. I. Klein.]—Attempts have been made to prepare salts of acetonitric acid by acting on nitrates with acetic acid, and on acetates with nitric acid. In the cases of potassium, sodium, ammonium, calcium, strontium, barium, magnesium, copper, and lead, no derivatives were obtained in this way. Silver nitrate is soluble in glacial acetic acid, and from the solution long, colourless, homogeneous crystals separate. This *diargentic acetonitrate*, $N(OAc)_2(OAg)_2{\cdot}OH$, exhibits no definite melting point, but explodes when heated slowly to 172°.

When mercurous nitrate is boiled with acetic acid, solution takes place, and, on cooling, colourless, transparent crystals of *mercuric acetonitrate*, $N(OAc)_2(O_2Hg)\cdot OH$, separate. This salt melts at 205°, and undergoes no change when heated at 110°. The silver salt decomposes easily in the air, but the mercuric salt is much more stable. The mercuric salt is insoluble in alcohol and ether, but is soluble in acids.

No esters of acetonitric acid are formed by the interaction of esters of nitric acid and acetic acid, or by the action of acetic acid on nitric esters, or of nitric acid on acetic esters. J. McC.

A New Fatty Acid. γγγ-Trimethylbutyric Acid [γγ-Dimethylvaleric Acid]. CHARLES MOUREU and RAYMOND DELANGE (*Bull. Soc. chim.*, 1903, [iii], 29, 664—666).—γγ-Dimethylvaleric acid, prepared as already described (this vol., i, 314), has sp. gr. 0·9129 at 20° and 0·9238 at 0°; the amide (*loc. cit.*) crystallises in rectangular lamellæ. T. A. H.

Amylchloroacrylic Esters [β-Chloro-Δ^α-octenoic Esters]. CHARLES MOUREU and RAYMOND DELANGE (*Bull. Soc. chim.*, 1903, [iii], 29, 677—678. Compare Abstr., 1901, i, 360).—When a solution of amylpropiolic acid in ethyl alcohol is saturated with hydrogen chloride, there is formed *ethyl β-chloro-Δ^α-octenoate*, $C_5H_{11}\cdot CCl{:}CH\cdot CO_2Et$, a colourless oil which boils at 123—128° under 18 mm. pressure. The chlorine atom is assumed to be in the β-position in this substance, since, on treatment with potassium hydroxide in alcohol, methyl amyl ketone is formed, whereas the α-substituted acid would, with this reagent, give rise to normal heptaldehyde. T. A. H.

Nitrates of Hydroxy-acids. H. DUVAL (*Bull. Soc. chim.*, 1903, [iii], 29, 678—680. Compare this vol., i, 603).—From the crude product obtained by the action of nitric acid on glycollic acid there has been isolated, in addition to the nitrate of glycollic acid (*loc. cit.*), *acetoxyacetic acid nitrate*, $NO_2\cdot O\cdot CH_2\cdot CO\cdot O\cdot CH_2\cdot CO_2H$, a yellow oil soluble in water and alcohol, but insoluble in benzene. A similar condensation appears to be produced by the action of nitric acid on lactic and α-hydroxybutyric acids.

Malic acid nitrate, similarly prepared, crystallises in colourless needles, melts and decomposes at 115°, is soluble in water and alcohol, but insoluble in benzene and light petroleum. T. A. H.

Labile and Stable Crotonolactones. EMIL ERLENMEYER, jun. (*Ber.*, 1903, 36, 2523—2525).—Thiele has shown (Abstr., 1899, i, 611) that γ-ketonic acids yield first labile βγ- and then stable αβ-unsaturated crotonolactones,

$$R\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot OH \longrightarrow R\cdot C{<}{\begin{matrix}CH\cdot CH_2\\ | \\ O{-}CO\end{matrix}} \longrightarrow R\cdot CH{<}{\begin{matrix}CH{:}CH\\ | \\ O{-}CO\end{matrix}},$$

whilst in the α-oxylactones the isomeric change, if it takes place, is from the αβ- to the βγ-unsaturated lactone (compare this vol., i, 419). Proof of this has been obtained (jointly with LATTERMANN) in the case

of the *a-oxylactone*, $CO<\begin{matrix}CO\cdot CHPh \\ O-CH\cdot C_6H_4\cdot OMe\end{matrix}$, prepared from anisaldehyde and phenylpyruvic acid, which is reduced by zinc dust and acetic acid to two isomeric unsaturated lactones. The *labile* lactone $CO<\begin{matrix}CH:CPh \\ O-CH\cdot C_6H_4\cdot OMe\end{matrix}$, melts at 105°, is unsaturated in the $\alpha\beta$-position, and is converted by heating with benzaldehyde and aniline only into the stable isomeride. The *stable* lactone, $CO<\begin{matrix}CH_2\cdot CPh \\ O-C\cdot C_6H_4\cdot OMe\end{matrix}$, melts at 122°, is unsaturated in the $\beta\gamma$-position, and condenses with benzaldehyde to yield the *benzylidene*-derivative,

$$CO<\begin{matrix}C(CHPh)\cdot CPh \\ O-\!\!-\!\!-\!\!-C\cdot C_6H_4\cdot OMe\end{matrix},$$

which forms orange-yellow needles and melts at 195°. T. M. L.

Action of Ammonia on a Mixture of Two a Oxyacids. EMIL ERLENMEYER, jun. (*Ber.*, 1903, 36, 2525—2526).—By the action of ammonia on a mixture of glyoxylic and pyruvic acids, aceturic acid, $CH_3\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, was obtained as a condensation product from the pyruvic acid only. [A syrupy acid was obtained which might contain also the mixed condensation product.] Similarly, a mixture of pyruvic and phenylpyruvic acids gave only phenylacetylphenylalanine, $CH_2Ph\cdot CO\cdot NH\cdot CHPh\cdot CO_2H$. T. M. L.

***iso*Nitrosomalonic Esters and their Transformation into Mesoxalic Esters.** LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1903, 137, 196—198).—*Ethyl* iso*nitrosomalonate* is obtained by passing a current of methyl nitrite into a mixture of ethyl malonate and sodium ethoxide at 20—25°, distilling off the alcohol, and treating the residue first with water, then with hydrochloric acid; the ester is extracted with ether and purified by distillation under diminished pressure. It is a colourless, viscid liquid which boils at 172° under 12 mm. pressure, has a sp. gr. 1·206 at 4°/0°; it is insoluble in water, but soluble in the ordinary organic solvents. If in the preparation the residue, after the alcohol has been evaporated, is left to itself, white needles of the *hydrogen* salt, $NOH:C(CO_2Et)_2 + NONa:C(CO_2Et)_2$, separate; this salt is easily dissociated by water. If a current of nitrogen peroxide be passed through the ester at 0°, vigorous action takes place. When the product is distilled under diminished pressure (12 to 15 mm.), ethyl mesoxalate and ethyl nitromalonate are obtained. The nitrogen peroxide therefore exerts two actions: (1) transformation of the oxime group into a ketonic group, and (2) direct oxidation.

Methyl iso*nitrosomalonate*, prepared in the same way, is a liquid which boils at 168° under 16 mm. pressure and crystallises when cooled. After recrystallisation from a mixture of ether and light petroleum it forms slender, white needles which melt at 67°. If water is added to the alkaline alcoholic solution in this preparation, crystals of the salt $NONa:C(CO_2Me)_2,2H_2O$ are deposited. The principal product of the action of nitrogen peroxide on methyl *iso*nitrosomalonate is methyl mesoxalate and its hydrate, which crystallises from a mixture

of ether and light petroleum in tabular crystals melting at 81°. At the same time a small quantity of methyl nitromalonate is formed.

J. McC.

Chitonic and Chitaric Acids. Emil Fischer and Edward Andreae (*Ber.*, 1903, 36, 2587—2592. Compare Fischer and Tiemann, Abstr., 1894, i, 167).—When dried at 140° the calcium salt of chitonic acid has the formula $(C_6H_{11}O_7)_2Ca$. At this temperature in an exhausted receiver over phosphoric oxide it loses 2 molecules of water; thus the salt has the formula, $(C_6H_9O_6)_2Ca,2H_2O$, and chitonic acid, $C_6H_{10}O_6$, that is, it is the anhydride of a hexonic acid. When heated with acetic anhydride and sodium acetate, it forms an acid compound, $C_8H_8O_5$, *acetoxymethylpyromucic acid*, which melts at 115—117° (corr.), has a bitter taste and crystallises from chloroform in needles or prisms. When hydrolysed with barium hydroxide, it is converted into the hydroxymethylpyromucic acid, melting at 165—167°, described by Hill and Jennings (*Amer. Chem. J.*, 1893, 15, 181). Similarly, chitaric acid is converted into acetoxymethylpyromucic acid, and thus both it and chitonic acid are represented by the structural formula, $\begin{array}{l}HO\cdot CH\cdot CH(CO_2H)- \\ \quad\;\; | \\ HO\cdot CH\cdot CH(CH_2\cdot OH)\end{array}\!\!>O$, and differ from one another with respect to the spatial arrangement of the hydroxyl groups. This makes it probable that *iso*saccharic acid and chitose are also both hydrofurfuran derivatives. E. F. A.

Action of Hypophosphorous Acid on Diethyl Ketone and on Acetophenone. Charles Marie (*Compt. rend.*, 1903, 137, 124—125. Compare this vol., i, 328, 379).—Diethyl ketone (3 to 4 mols.) is boiled with hypophosphorous acid (1 mol.) in a reflux apparatus, the excess of ketone is distilled off, and the residue is converted into the *lead salt*, $Pb[COEt_2,H_2PO_2]_2$. The lead salt is decomposed in aqueous suspension with hydrogen sulphide, when the *acid* is obtained as a colourless syrup which does not solidify at $-20°$. On oxidation with bromine or mercuric chloride, it gives the oxyphosphinic acid, Et_2CO,H_3PO_3; this is soluble in water, alcohol, acetone, and ethyl acetate, but insoluble in benzene or chloroform. Its silver salt is insoluble in water.

If acetophenone (3 mols.) is heated on the water-bath with hypophosphorous acid, and the mixture treated with lead carbonate, the insoluble *lead salt*, $Pb[COMePh,H_2PO_2]_2$, is formed. When decomposed with hydrogen sulphide, it gives the *acid*, $COMePh,H_3PO_2$, as a syrup which slowly solidifies, and melts at 70°. When oxidised with mercuric chloride, it gives the oxyphosphinic acid, $COMePh,H_3PO_3$ (m. p. 170°), but when oxidised with bromine, the product isolated is $COMePh,H_3PO_3,HBr$, which melts at 190°. J. McC.

Conversion of Methyl Nonyl Ketone into the Isomeric Ethyl Octyl Ketone. C. Mannich (*Ber.*, 1903, 36, 2551—2553).—The hydrocarbon $C_{11}H_{20}$ (this vol., i, 674), which does not react with ammoniacal silver nitrate is Δ^{β}-*undecinene*, $CMe\!:\!C\cdot C_8H_{17}$, as, on oxidation with

cold 4 per cent. permanganate solution, it yields acetic and pelargonic acids. It is a colourless oil with a disagreeable odour, distils at 199—201° under atmospheric, or at 81·5° under 10·5 mm. pressure, and is fairly readily volatile even at the ordinary temperature. In chloroform solution it combines with two atoms of bromine yielding an oily *dibromide*, $CMeBr{:}CBr{\cdot}C_8H_{17}$, distilling at 137—139° under 11 mm. pressure. When Δ^β-undecinene is poured into ice-cold 94 per cent. sulphuric acid, it absorbs the elements of water, and yields a mixture of two ketones, namely, methyl nonyl ketone (18 per cent.) and ethyl octyl ketone (82 per cent.). The two ketones can be separated by the aid of sodium hydrogen sulphite, as the methyl nonyl ketone forms an additive compound and the ethyl octyl ketone does not.

Ethyl octyl ketone is a colourless liquid with a pleasant odour, it distils at 104—106° under 11 mm. pressure, solidifies at 4·5°, and reacts with hydroxylamine and semicarbazide hydrochloride. The *oxime* is oily, and the *semicarbazone* has no sharp melting point. When oxidised with chromic mixture, it yields *n*-octoic acid.

As Δ^β-undecinene is obtained from methyl nonyl ketone (*loc. cit.*), it affords a simple method of transforming the ketone into the isomeric ethyl octyl ketone. J. J. S.

Condensation of Higher Aliphatic Ketones to Compounds of the Type of Mesityl Oxide. Hermann Thoms and C. Mannich (*Ber.*, 1903, 36, 2555—2558).—When methyl nonyl ketone is saturated with hydrogen chloride and kept for some 6 weeks, condensation occurs. The mass is washed with water and potassium carbonate solution, dried and fractionated under reduced pressure. A considerable amount of hydrogen chloride is evolved during the distillation, and an *unsaturated ketone*, $C_9H_{19}{\cdot}CMe{:}CH{\cdot}CO{\cdot}C_9H_{19}$, passes over at 214—216° under 10 mm. pressure. It is a colourless, oily liquid with a faint odour, and has sp. gr. 0·8514 at 15°. It readily combines with hydrogen chloride to form an oily compound, which decomposes into its components on distillation even under reduced pressure.

The *oxime, phenylhydrazone,* and *semicarbazone* have only been obtained in the form of oils. The *picrate* of its *aminoguanidine derivative*, $C_{29}H_{49}O_7N_7$, melts at 125—126°.

When boiled with 60 per cent. sulphuric acid, the ketone is hydrolysed to methyl nonyl ketone. On oxidation with permanganate it yields decoic and carbonic acids with a small amount of acetic acid.

Methyl heptyl ketone condenses under the influence of hydrogen chloride to an *unsaturated ketone*, $C_7H_{15}{\cdot}CMe{:}CH{\cdot}CO{\cdot}C_7H_{15}$; it is difficult to obtain this free from chlorine, as it readily combines with hydrogen chloride, and the whole of this is not removed on distillation. The *picrate* of its *aminoguanidine derivative* melts at 130—131°.

J. J. S.

Transformation of Starch Paste. Léon Maquenne (*Compt. rend.*, 1903, 137, 88—90).—When a homogeneous starch jelly in an aseptic medium is kept for some days, the translucent mass becomes opaque, and finally deposits segregated nuclei. This change is due

to a transformation of the starch, which passes into the form of amylocellulose described by Brown and Heron. The transformed substance is not coloured by iodine, is not attacked by malt, and is only very slowly hydrolysed by boiling dilute solutions of mineral acids. On the other hand, it is easily soluble in solutions of potassium hydroxide, and the neutralised solution gives a blue coloration with iodine. This behaviour seems to indicate that the amylocellulose has a lactonic character, which is probably due to a partial dehydration of the original starch molecule.

The transformation is progressive; its velocity slowly diminishes, and even after 20 days is not complete. The transformation is purely chemical, and entirely independent of enzymes or micro-organisms.

The velocity of the change appears to be greater if the starch jelly has not been heated. J. McC.

β-Aminoundecane and β-Aminononane. HERMANN THOMS and C. MANNICH (*Ber.*, 1903, **36**, 2554—2555).—These two compounds are obtained by the reduction of the oximes of methyl nonyl ketone and methyl heptyl ketone with sodium in a mixture of alcohol and acetic acid.

β-Aminoundecane is a light, colourless liquid distilling at 113—114° under 26 mm. pressure. It has strongly alkaline properties, and readily absorbs carbon dioxide. The *platinichloride*, $C_{22}H_{50}N_2,H_2PtCl_6$, crystallises in plates or needles, turns black at 240°, and is only very sparingly soluble in cold water. The *picrate* melts at 111°.

β-Aminononane distils at 69—69·5° under 11 mm. pressure. Its *hydrochloride* is extremely hygroscopic and is soluble in alcohol, ether, or acetone. The *platinichloride*, $C_{18}H_{42}N_2,H_2PtCl_6$, turns black at 210—220° when quickly heated, and the *picrate* melts at 108·5—109·5°. J. J. S.

Action of Ammonia on the Ethylene Oxide of β-o-cyclo-Hexanediol [esoAnhydride]. LÉON BRUNEL (*Compt. rend.*, 1903, **137**, 198—199. Compare this vol., i, 338, and preceding abstract).—When the *eso*anhydride, $C_6H_{10}\!:\!O$, is heated in a sealed tube with a large excess of ammonia, *orthoaminocyclohexanol*, $OH{\cdot}C_6H_{10}{\cdot}NH_2$, is obtained as a colourless, crystalline mass with an odour of piperidine, which is not affected by light and is soluble in water and the ordinary solvents. It melts at 66° and boils at 219°; it is extremely hygroscopic and readily absorbs carbon dioxide. Its *hydrochloride* forms white needles which melt at 175°, and its *nitrate* melts at 144°.

If less ammonia is used, *dihydroxycyclohexylamine*, $NH(C_6H_{10}{\cdot}OH)_2$, is formed as well. This is obtained in two forms when the *eso*anhydride is heated in a sealed tube with twice its volume of an alcoholic solution of ammonia. On cooling, β_1-*dihydroxycyclohexylamine* crystallises out in colourless leaflets, which melt at 153°, and are sparingly soluble in water or alcohol. Its *hydrochloride* melts at 266°. It forms a *nitrosamine*, $NO{\cdot}N(C_6H_{10}{\cdot}OH)_2$, which crystallises in yellow prisms and melts at 148°. The alcoholic solution contains β_2-*dihydroxycyclohexylamine*, which on evaporating the alcohol,

warming the residue with benzene, and cooling, separates in slender, colourless needles which melt at 114°. The *hydrochloride* melts at 192°, and the *nitrosamine* at 171°. J. McC.

Preparation of Secondary Amides. J. Tarbouriech (*Compt. rend.*, 1903, **137**, 128—130).—The author has prepared some secondary amides (1) by the action of acids on nitriles, and (2) by the action of acid chlorides on primary amides in sealed tubes.

n-*Dibutyramide* is obtained by heating together in a sealed tube *n*-butyrylnitrile and *n*-butyric acid at 205°; the product is subjected to distillation, and when the thermometer reaches 200° the heating is stopped; the residue solidifies on cooling and the dibutyramide is recrystallised from alcohol. The same compound is formed when molecular quantities of *n*-butyramide and *n*-butyryl chloride are heated in a sealed tube at 120—130° for 6 hours. It can be distilled under diminished pressure and melts at 107°.

*Di*iso*butyramide*, prepared in the same ways, forms large, colourless crystals, melts at 173—174°, and is almost insoluble in cold water or alcohol, but easily soluble in ether.

*Di*iso*valeramide* forms slender, white needles, and melts at 94°. *Di*-n-*valeramide* is a white, crystalline substance melting at 100°, sparingly soluble in cold alcohol, but easily in ether.

In the preparation of these amides, ammonium chloride is frequently formed in small quantity at the same time as a very small amount of a tertiary amide. J. McC.

[Physico-chemical Constants of] Organic Amides. (Constitution of Nitrosoalkylurethanes, Acid Amides, Anthranil, Regularities in the Boiling Points of Acid Amides, Analogy between Formylamines and Nitrosoamines.) Otto Schmidt (*Ber.*, 1903, **36**, 2459—2482).—The following compounds were examined:

I. Monoacylamines. (*a*) *Primary.*

	M. p.	t.	$d^{t/4}$.	n^t_D.	$\mathfrak{M}_D$.
Methyl carbamate	57—58°	55·6°	1·1361	1·41253	16·448
Ethyl ,,	49	52·0	1·0560	1·41439	21·078
iso*Butyl* ,,	64—65	76·2	0·9556	1·40978	30·320
iso*Amyl* ,,	64	70·6	0·9438	1·41754	34·945

(*b*) *Secondary.*

	B. p.	p.	t.	$d^{t/4}$.	n^t_D.	$\mathfrak{M}_D$.
*Formyl*iso*butylamine*	111°	12 mm.	17°	0·9092	1·43957	29·262
*Formyl*iso*amylamine*	123·5—124	10	13·2	0·9049	1·44513	33·833
Formanilide (m. p. 47°)	166	14	21	1·13958	1·58786	35·728
			25·6	1·13811	1·58763	35·775
			17·3	1·14366	1·59012	35·711
Methyl anthranilate	126·2—126·8	12	18·6	1·16822	1·58435	43·280
Ethyl anthranilate	137·5—138	14	20·7	1·11792	1·56487	47·647
Methyl formylanthranilate (m. p. 42—43°)	169·8—170	13	37·6	1·23336	1·57776	48·146
Methyl methylcarbamate	64 — 65	14	20·6	1·06405	1·41584	20·982
Ethyl methylcarbamate	79·8— 80·6	14·5	18·9	1·00874	1·42004	25·842
Ethyl ethylcarbamate	74 — 75	14	19·6	0·97645	1·42254	30·484

(*b*) *Secondary*—continued.

	B. p.	*p.*	*t.*	$d^{t/4}$.	*n* .	$\mathfrak{M}_D$.
Ethyl iso*butylcarbamate*	95 — 96°	15 mm.	16·8	0·94452	1·43008	39·665
Ethyl iso*amylcarbamate*	122 —123	22	20·9	0·93258	1·43267	44·282
Ethyl phenylcarbamate (m. p. 53°)	152	14	30·4	1·10639	1·53764	46·626
iso*Formylanilinomethyl ether*	83 — 84	15	23·5	1·03474	1·53821	40·823
iso*Formanilinoethyl ether.*	107 —108	23	17·4	1·0090	1·52978	45·600

(*c*) *Tertiary.*

Dipropylformylamine	96 — 97	14	19·8	0·8892	1·44094	38·305
*Di*iso*butylformylamine*	109 —110	15	16·6	0·87472	1·44295	47·583
*Di*iso*amylformylamine*	132 —132·6	13	20·4	0·86688	1·44556	56·863
			17·5	0·86876	1·44617	56·805
Formylmethylaniline	124·9—125·2	13	27·4	1·08930	1·55902	40·017
			23·0	1·09280	1·55780	39·815
Formylethylaniline	89·5— 91	14	22	1·05422	1·54313	44·561
Formyldiphenylamine (m. p. 72·2—72·6°)	189·5—190·5	13 ; was examined in toluene solution.				
Toluene	—	—	15·2	0·8702	1·49894	—
Solution (25·685 per cent.)			15·3	0·9315	1·52533	60·24
Ethyl diethylcarbamate	62 — 63	14	20·9	0·92824	1·42017	39·545
*Ethyl di*iso*amylcarbamate*	129 —130	14	22·8	0·88038	1·43292	67·597
Ethyl phenylmethylcarbamate	127 —128	13	17·8	1·07585	1·51734	50·365
Ethyl phenylethylcarbamate	130 —130·5	14	18·4	1·04529	1·50765	55·005
Nitrosodipropylamine	95 — 95·6	18	16·8	0·9182	1·44535	37·708
*Nitrosodi*iso*amylamine*	132·4—132·8	14·5	15·6	0·88668	1·45029	56·406
			16·0	0·88720	1·45013	56·356
			15·6	0·88720	1·45036	56·380
Nitrosomethylaniline	120·9—121·5	13	25·5	1·1253	1·57567	39·976
Nitrosoethylaniline	119·5—120	15	22·0	1·0858	1·55947	44·636
Nitrosodiphenylamine (m. p. 67·2—67·6°) was examined in toluene solution.						
Solution (25·493 per cent.)			14·4	0·93449	1·52570	59·75

(*d*) *Other Compounds.*

Anthranil	90·2	14·5	13·2	1·18810	1·58723	—
Phenylcarbimide	—	—	25·9	1·08870	1·53412	33·990

II. Diacylamines.

Methyl nitrosomethylcarbamate	59·3—60	14	24·6	1·20419	1·44048	25·848
Nitrosomethylurethane	65 —65·5	13	18·8	1·13144	1·43852	30·659
Nitrosoethylurethane	69 —70	15	19·3	1·0854	1·43533	35·123

The constitution of acid amides has been studied by Auwers, Brühl, Claisen, and by Hantzsch and Dollfus (Abstr., 1902, i, 223). The latter maintain the correctness of the normal formulation, a result with which the author is also in agreement. The reactivity of the acyl grouping in the acylamines was also studied. Although amidine formation occurs with great ease in the case of acylanthranils, it was not found possible to obtain other acylamines with an equal reactivity. Ordinary monoacylamines are inert in this respect; thus, phenylhydr-

azine does not condense with acetanilide, whilst formanilide, when condensed with β-naphthol, yields only small quantities of a substance melting above 200°. Accordingly, arylalkylcarbamic chlorides are stable; by the action of phosphorus oxychloride, for instance, on phenylmethylurethane, the stable phenylmethylcarbamic chloride (m. p. 88—89°) was prepared.

With regard to the constitution of nitrosoalkylurethanes, the author's refractometric results lead him to the conclusion that nitrosoalkylurethanes are true nitrosoamines; this agrees with Hantzsch's conception (Abstr., 1900, i, 86), and is opposed to Brühl's (Abstr., 1900, i, 210).

From the values of the molecular refraction of the various acylamines examined, the refractometric constant of the acyl grouping can be calculated. Since the values in primary, secondary, and tertiary aliphatic formylamines and urethanes are practically the same, and since the tertiary compounds can possess the normal structure only, the normal structure may also be assigned to the primary and secondary compounds. With secondary, aromatic acylamines, the refractometric value of the acyl group is higher than with the tertiary compounds. From the values obtained with formanilide, on the one hand, and the iminoethers, *iso*formanilino-methyl and -ethyl ethers on the other, it is concluded that formanilide has the normal structure. In agreement with this, formanilide, when heated in a sealed tube for 4 hours at 100° with phenyl*iso*cyanate, gives an almost quantitative yield of *formyldiphenylcarbamide*, melting and decomposing at 103—104°, and giving diphenylcarbamide by the action of boiling hydrochloric acid. When hydrogen chloride is led into a solution of formanilide in dry xylene, the hydrochloride, NHPh·CHO,HCl, is formed; it is unstable and parts readily with hydrogen chloride.

According to Anschütz and Schmidt, anthranil has the constitution $C_6H_4<\begin{matrix}CO\\|\\NH\end{matrix}$ (this vol., i, 56), whilst Bamberger prefers $C_6H_4<\begin{matrix}CH\\|\\N\end{matrix}>O$ (this vol., i, 432). From the comparison of the refractometric values of anthranil, formanilide, and phenylcarbimide, the former constitution is justified.

Various regularities in the boiling points of amides are indicated. The hydrogen atom attached to nitrogen in a secondary or primary acylamine has the same character as the hydrogen of a hydroxyl group.

In physical properties, tertiary formylamines are very closely allied to their corresponding nitrosoamines, the boiling points, refractometric constants, and molecular volumes of various compounds are quoted. In some cases, as, for instance, with formyldiphenylamine and nitrosodiphenylamine, the crystallographic structure is nearly identical.

The molecular refraction of nitrosoaniline is calculated, and found to agree with that of formanilide. Like true nitrosoamines, formanilide is comparatively inert, whilst the ethers derived from the *iso*-form are much more chemically active. Phenylhydrazine was found by the author to condense with *iso*formanilinomethyl ether to form the corresponding diazohydrazide. A. McK.

Constitution of Allyl Cyanide. ROBERT LESPIEAU (*Compt. rend.*, 1903, 137, 262—263).—By the action of a chloroform solution of bromine on a chloroform solution of dried allyl cyanide at $-14°$ to $-10°$ for 9 hours, hydrogen bromide is evolved and the residue can be separated into a fraction boiling at 60—100° and one boiling at 125—135° under 13 mm. pressure. The latter consists essentially of $\beta\gamma$-dibromobutyronitrile, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CN$ (compare this vol., i, 547). The fraction of lower boiling point was refractionated and the molecular weight of the various fractions determined; it apparently consists of a monobromo-substitution product of allyl cyanide ($C_4H_5BrO_2$). The author concludes that the constitution of allyl cyanide is best represented by the formula $CH_2{:}CH{\cdot}CH_2{\cdot}CN$.

J. McC.

Double Cyanides of Zinc with Potassium and with Sodium. WILLIAM J. SHARWOOD (*J. Amer. Chem. Soc.*, 1903, 25, 570—596).—In the precipitation of gold and silver by the addition of zinc to the solutions obtained in the cyanide process of extraction, a certain amount of zinc is dissolved. The present investigation was undertaken in order to ascertain the nature of the zinc compound thus produced.

When an alkaline solution containing the cyanides of zinc and potassium is concentrated, potassium zinc cyanide, $K_2Zn(CN)_4$, is obtained, which crystallises in regular octahedra, and is soluble to the extent of 11 grams in 100 c.c. of water at 20°, and is nearly insoluble in alcohol. The same salt is formed by the action of potassium cyanide on zinc oxide or of potassium hydroxide on excess of zinc cyanide.

If a solution of sodium and zinc cyanides is concentrated, a hydrated form of sodium zinc cyanide, $NaZn(CN)_3$, is produced, which crystallises with difficulty, and is partially decomposed by the addition of water with precipitation of a basic zinc cyanide. This salt does not seem to exist in the solution, for the mother liquor contains Zn : CN approximately in the ratio 1 : 4. When dilute solutions of sodium cyanide react with zinc cyanide or zinc oxide, or when sodium hydroxide reacts with an excess of zinc cyanide, the ratio of zinc to cyanogen in the resulting solution is approximately that required by the compound $Na_2Zn(CN)_4$.

When $N/10$ solutions of the hydroxides of sodium or potassium are shaken with zinc oxide, very little of the latter is dissolved, and the zinc oxide formed is largely decomposed on boiling.

Zinc cyanide is dissolved by dilute solution of potassium cyanide with the formation of a solution of double cyanide, $K_2Zn(CN)_4$, which is little affected by boiling or by the presence of carbonic acid. A similar solution is obtained by the action of sodium cyanide on zinc cyanide.

Zinc oxide is dissolved by $N/10$ potassium cyanide solution in the proportion of 3 mols. of the former to 10 mols. of the latter; on boiling the solution thus formed, decomposition occurs with precipitation of zinc oxide. Dilute solutions of sodium cyanide behave in a similar manner.

Zinc cyanide (1 mol.) is dissolved by a dilute solution of potassium hydroxide (2 mols.) with formation of a solution which is decomposed on heating, zinc oxide being precipitated and potassium hydroxide remaining in the solution. A solution can be also prepared containing zinc cyanide and potassium hydroxide in molecular proportion, but zinc oxide soon begins to separate. Sodium hydroxide reacts in similar manner with zinc cyanide.

The solvent action of a solution of potassium zinc cyanide on gold is less than that of a simple solution of potassium cyanide containing half the amount of cyanogen per unit volume. If potassium hydroxide is added to such a solution, the solvent power is greatly increased. It is evident, therefore, that potassium zinc cyanide in dilute solutions is partially decomposed by potassium hydroxide with formation of potassium cyanide. E. G.

Prussian and Turnbull's Blues. A New Class of Complex Cyanides. PAUL CHRÉTIEN (*Compt. rend.*, 1903, **137**, 191—194).—When hydroferricyanic acid spontaneously decomposes at about 20°, *hydrodiferrocyanic acid*, $HFe_2(CN)_6,3H_2O$, is formed. The decomposition is greatly assisted by the presence of bromine. The liquid soon gelatinises, but the acid can be again obtained in a soluble form by dialysis. When treated with alkaline salts hydrogen salts of the type $RH[Fe_2(CN)_6]_2,6H_2O$ are formed; the silver salt has $7H_2O$. With salts of barium, manganese, cobalt, or iron, coagulation of the acid takes place and no salt is produced.

The following thermochemical values have been determined: $HFe_2(CN)_6,3H_2O$ (solid) + 4KOH (dissolved) = $K_4Fe(CN)_6$ (dissolved) + $Fe(OH)_3$ (solid) + 25·4 Cal.; from this it is deduced that the heat of formation of the solid acid is 122·15 Cal. This value is in good agreement with that obtained from the heat changes involved in the decomposition of the soluble Prussian blues. J. McC.

Diazomethane. RUDOLF WEGSCHEIDER and HEINRICH GEHRINGER (*Monatsh.*, 1903, **24**, 364—366).—In the preparation of various acid esters by the aid of diazomethane, it was observed that the yield of ester formed was greater than that calculated from the amount of diazomethane used. The diazomethane was employed in ethereal solution, the strength of which was estimated by titration with standard iodine solution according to von Pechmann (Abstr., 1894, i, 438), who supposed that the action took place according to the equation $CH_2N_2 + I_2 = CH_2I_2 + N_2$. The authors have studied the esterification of benzoic acid by diazomethane. Accepting von Pechmann's view, and taking a quantity of benzoic acid corresponding with $C_7H_6O_2 + CH_2N_2 = C_8H_8O_2 + N_2$, they find that the benzoic acid is completely esterified, but that some diazomethane remains unattacked. In the one experiment quoted, the diazomethane used esterified twice as much benzoic acid as it should do according to the above equations. A. McK.

Action of Nitrogen Peroxide on Organo-Magnesium Compounds. HEINRICH WIELAND (*Ber.*, 1903, **36**, 2315—2319).—Grignard has shown (Abstr., 1902, i, 142) that, by the action of magnesium-alkyl iodides, carbon dioxide may be converted into carboxylic acids

and sulphur dioxide into sulphinic acids. With the object of preparing the corresponding nitrogen acids, the author has studied the action of magnesium-alkyl iodides on nitrogen peroxide. Instead, however, of obtaining acids of the type R·N:O·OH, he obtained $\beta\beta$-dialkylated hydroxylamines of the type NRR·OH, the same products which result from nitroparaffins and organic zinc or magnesium compounds.

A violent action ensues when nitrogen peroxide is passed into an ethereal solution of the magnesium compound at the ordinary temperature. A strongly cooled solution of magnesium in ethyl iodide was added very gradually to an ethereal solution containing 5 per cent. of nitrogen peroxide, the latter solution being immersed in a freezing mixture. After careful decomposition of the resulting double compound with water and subsequent extraction with ether, the base *diethylhydroxylamine* was obtained, which was converted into its *oxalate*: this crystallises from methyl alcohol in needles melting at 138° (compare Dunstan and Goulding, Trans., 1899, **75**, 800). The *hydrochloride* is deliquescent and melts at 63°. The free base, obtained from the oxalate or the hydrochloride, boils at 76° under 86 mm. pressure, and has the properties assigned to it by Dunstan and others. Further, it readily reduces alkaline copper and silver solutions as well as gold and platinic chlorides.

The action of nitrogen peroxide on magnesium phenyl bromide is also violent, and is being further studied by the author in the hope of isolating diphenylhydroxylamine. A. McK.

Action of Sulphur on Organo-Magnesium Compounds. Henri Wuyts and G. Cosyns (*Bull. Soc. chim.*, 1903, [iii], **29**, 689—693. Compare Bodroux, this vol., i, 121, 249, 521).—When magnesium ethyl iodide in ethereal solution is treated with sulphur and the resulting product decomposed with water, hydrogen sulphide is evolved, and there is formed ethyl mercaptan and small quantities of ethyl disulphide and of an unidentified oily sulphur compound. Magnesium phenyl bromide reacts with sulphur under these conditions to form thiophenol, diphenyl sulphide, and diphenyl disulphide. By reducing the crude product with powdered zinc and dilute hydrochloric acid, a yield of 66 per cent. of thiophenol can be obtained, and the reaction is recommended as a method of preparing this substance.

It is suggested that the first products of reaction in these cases are compounds of the type RSMgX and RS_2MgX, which are decomposed by water, giving rise to substances of the type RSH and RS_2H respectively, which interact with each other to form the sulphides RS_2R and RS_3R.

Selenium and tellurium react similarly with organo-magnesium compounds. T. A. H.

***cyclo*Hexane and its Chloro-derivatives.** Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1903, **137**, 240—242).—When benzene is hydrogenated by the catalytic process, cyclo*hexane*, C_6H_{12}, is produced identical with that which occurs in Caucasian petroleum. It melts at 6·5°, boils at 81° under 755 mm. pressure, has a sp. gr. 0·7843 at 13·5° and 0·7551 at 44·6°, and n_α 1·42777, n_β 1·43531, n_γ 1·43972. The existence of the benzene nucleus in it has been

established by the fact that with bromine it gives tetrabromobenzene. When passed over reduced nickel at 270—280°, it gives benzene and methane ($3C_6H_{12} = 2C_6H_6 + 6CH_4$).

When chlorine is passed through it at 0° substitution takes place, and the action is energetic. The presence of iodine chloride or antimony chloride has no effect on the action, but if aluminium chloride be present condensed products are obtained. After chlorination, the product was washed with dilute potassium hydroxide solution, then dried and fractionated under 50 mm. pressure, when di-, tri-, and tetrachloro-derivatives were separated.

*Chloro*cyclo*hexane* is a colourless liquid with a pleasant odour, which boils at 141·6—142·6° under 749 mm. pressure, and has a sp. gr. 1·0161 at 0°/0°, and 0·9976 at 22°/0°. When boiled with alcoholic potassium hydroxide it gives *cyclo*hexene.

*Dichloro*cyclo*hexanes* were obtained in two fractions under 50 mm. pressure. Of the first, the one boiling at 105·4—106·4° has a sp. gr. 1·2056 at 0°/0°, and at 106·4—107·4° has a sp. gr. 1·2060 at 0°/0°. Under 761 mm. pressure, it boils at 189° with decomposition and evolution of hydrogen chloride. When cooled in solid carbon dioxide it solidifies, and melts at 93°. When heated for a long time with alcoholic potassium hydroxide it gives naphthylene chloride, C_6H_9Cl, which gives a red coloration with sulphuric acid. At the same time a small quantity of a hexaterpene, C_6H_8, is formed.

The second liquid boils at 112·4—113·4° under 50 mm. pressure, and at 196° under 760 mm. pressure, and has a sp. gr. 1·2222 at 0°/0°; this is probably the 1 : 2 derivative.

Two liquid *trichloro*cyclo*hexanes* have been isolated. They possess a disagreeable odour. The first boils at 139·5—141·5° under 50 mm. and at 221° with much decomposition at 745 mm. pressure, and has a sp. gr. 1·3535 at 0°/0°. The second boils at 143·5—145·5° under 50 mm. and at 226° with decomposition under 745 mm. pressure, and has a sp. gr. 1·3611 at 0°/0°. A solid *trichloro*cyclo*hexane*, which was also obtained, forms colourless crystals which are very soluble in chloroform, melts at 66°, boils at 150·4—151·4° under 50 mm. pressure, and has a sp. gr. 1·5103 at 0°/0°. When heated at 100° in a sealed tube with alcoholic potassium hydroxide, it loses 3 mols. of hydrogen chloride and gives benzene; it is probably the 1 : 3 : 5-derivative.

The continued action of chlorine in the sunlight on *cyclo*hexane leads to *tetrachloro*cyclo*hexane*. This crystallises from chloroform in long prisms, melts at 173°, and can be volatilised, has a sp. gr. 1·6404 at 0°/0°, and when heated with alcoholic potassium hydroxide loses 3 mols. of hydrogen chloride and gives chlorobenzene. The liquid from which this compound is deposited gives a residue, and by fractionally distilling this under 50 mm. pressure a liquid *tetrachloro*cyclo*hexane* is obtained boiling at 170·5—172·5°. J. McC.

Action of Sodium on Carbon Tetrachloride and Chlorobenzene; Formation of Triphenylmethane and Hexaphenylethane. Jules Schmidlin (*Compt. rend.*, 1903, **137**, 59—60).—The action of sodium on a mixture of carbon tetrachloride and chlorobenzene in benzene solution is slow at the ordinary temperature, but

after about a day the reaction becomes violent. Triphenylmethane and hexaphenylethane were identified in the product, and were separated by acetic acid, in which the latter is insoluble. Hydrogen chloride is evolved during the reaction. In the first place triphenylchloromethane is formed: $3PhCl + CCl_4 + 6Na = Ph_3{:}C{\cdot}Cl + 6NaCl$, and then undergoes the actions: $Ph_3{:}C{\cdot}Cl + H_2 = Ph_3{\cdot}CH + HCl$ and $2Ph_3{:}C{\cdot}Cl + 2Na = 2NaCl + Ph_3{:}C{\cdot}C{:}Ph_3$. Diphenyl was isolated from the more volatile portions.

Tetraphenylmethane was not formed. J. McC.

Allylbenzene. August Klages (*Ber.*, 1903, **36**, 2572—2574).—A reply to Kunckell (this vol., i, 331). Allylbenzene has been prepared by the two methods previously described (this vol., i, 329, and Abstr., 1902, i, 666), and has been proved to possess the physical data previously given, namely, sp. gr. 0·9141 at 20°/4°, n_D 1·5497 at 12°, and boiling point 176—178° at 754 mm. These data agree with those given by Perkin (Trans., 1891, **59**, 1010), but not with Kunckell's numbers. This is due either to the presence of small amounts of *n*-propyl benzene in Kunckell's preparation or to the presence of an isomeric hydrocarbon, such as phenyltrimethylene, in the author's samples. J. J. S.

Phenylpropargylidene Chloride, $CPh{:}C{\cdot}CHCl_2$. Ernest Charon and Edgar Dugoujon (*Compt. rend.*, 1903, **137**, 125—128. Compare this vol., i, 472) —Phenylpropargylaldehyde was prepared by a modified form of Moureu and Delange's method (Abstr., 1901, i, 581). Ethyl formate dissolved in anhydrous ether was cooled to 0°, and the sodium derivative of phenylacetylene was added to it; acetic acid was then added in slight excess, then, after diluting with water, the aldehyde was extracted with ether. The chloro-derivative was obtained from the aldehyde by the action of phosphorus pentachloride. *Phenylpropargylidene chloride* is a colourless liquid which boils at 131—132° under 22 mm. pressure, does not solidify at −14°, and has a sp. gr. 1·2435 at 0°. In the air it slowly becomes yellow, but is much more stable than cinnamylidene chloride; it is only slowly decomposed by water. With chlorine, it gives a solid having the formula,

$$CHPhCl{\cdot}CHCl{\cdot}CHCl_2,$$

which boils at 165—167° under 28 mm. pressure, and is very stable in the air and under water. By the action of bromine in acetic acid or chloroform, the propargylidene compound gives slender needles of the bromide, $CHPhBr{\cdot}CHBr{\cdot}CHCl_2$, which are extremely stable.

The authors discuss the stability relationships of these compounds containing double and treble linkings. J. McC.

Certain Nitro-derivatives of Vicinal Tribromobenzene. C. Loring Jackson and Augustus H. Fiske (*Amer. Chem. J.*, 1903, **30**, 53—80).—3 : 4 : 5-Tribromo-1-nitrobenzene melts at 112°. When treated with dilute sodium methoxide, it is converted into 2 : 6-dibromo-4-nitroanisole, melting at 122°, which was first prepared by Körner (Abstr., 1876, i, 228) by the action of methyl iodide on the silver derivative of 2 : 6-dibromo-4-nitrophenol.

3 : 5-*Dibromo*-4-*methoxyazoxybenzene*, $ON_2(C_6H_2Br_2{\cdot}OMe)_2$, obtained by the action of a strong solution of sodium methoxide on 3 : 4 : 5-tribromonitrobenzene, crystallises from benzene in groups of yellowish-white needles, melts at 214°, and is soluble in chloroform or benzene; this compound may also be prepared by the action of sodium methoxide on 2 : 6-dibromo-4-nitroanisole. When 2 : 6-dibromo-4-nitroanisole is reduced with tin and hydrochloric acid, it is converted into 2 : 6-dibromo-4-anisidine, which melts at 64—65°.

By the action of a dilute solution of sodium ethoxide on 3 : 4 : 5-tribromonitrobenzene, 2 : 6-dibromo-4-nitrophenetole is obtained, which crystallises in white, slender needles, melts at 58—59°, and not at 108° as stated by Staedel (Abstr., 1883, 663), and is very soluble in ether, benzene, chloroform, or acetone. When 3 : 4 : 5-tribromonitrobenzene is treated with a strong solution of sodium ethoxide, 3 : 5-*dibromo*-4-*ethoxyazoxybenzene*, $ON_2(C_6H_2Br_2{\cdot}OEt)_2$, is produced, which crystallises from benzene in long, slender, yellowish-white needles, melts at 163°, and is soluble in chloroform; this substance may also be prepared by the action of sodium ethoxide on 2 : 6-dibromo-4-nitrophenetole. By the reduction of 2 : 6-dibromo-4-nitrophenetole with tin and hydrochloric acid, 2 : 6-dibromo-4-phenetidine is formed, which crystallises in white plates and melts at 107° instead of 67° as given by Staedel (*loc. cit.*); its *hydrochloride* was prepared and analysed.

When 3 : 4 : 5-tribromonitrobenzene is boiled with a dilute solution of potassium carbonate, very little action takes place, but by the action of sodium hydroxide, 2 : 6-dibromo-4-nitrophenol is produced.

3 : 4 : 5-*Tribromo*-1 : 2-*dinitrobenzene*, obtained by nitration of 3 : 4 : 5-tribromo-1-nitrobenzene, forms large, yellowish-white prisms, melts at 160°, and is readily soluble in benzene, chloroform, acetone, or glacial acetic acid. 2 : 3 : 4-*Tribromo*-6-*nitroanisole*, prepared by the action of dilute sodium methoxide on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene, crystallises from alcohol in white, slender needles, melts at 109—110°, and is freely soluble in ether, benzene, chloroform, or acetone. *Dibromonitrodimethoxybenzene*, $NO_2{\cdot}C_6HBr_2(OMe)_2$, formed by the action of boiling sodium methoxide solution on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene or on 2 : 3 : 4-tribromo-6-nitroanisole, crystallises in white, slender needles, melts at 81°, and is readily soluble in alcohol, ether, benzene, chloroform, or acetone.

2 : 3 : 4-*Tribromo*-6-*nitrophenetole*, $NO_2{\cdot}C_6HBr_3{\cdot}OEt$, obtained by the action of cold sodium ethoxide on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene, crystallises in small, white rosettes, melts at 74°, is freely soluble in ether, benzene, chloroform, or acetone, and on exposure to the air gradually becomes yellow and afterwards brown.

When 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene is boiled with aqueous sodium hydroxide, 2 : 3 : 4-*tribromo*-6-*nitrophenol* is produced, which crystallises in thick, yellow prisms, melts at 120—121°, and is readily soluble in chloroform, acetone, or hot benzene; the *sodium* and *silver* derivatives were prepared and analysed. By the action of methyl iodide on the silver salt, the corresponding anisole melting at 109° is produced.

Ethyl sodiomalonate reacts with 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene with formation of a red salt which is converted by acids into a *substance*,

probably $C_6HBr_2(NO_2)_2{\cdot}CH(CO_2Et)_2$, which melts at 103—104°. A similar red salt is produced by the action of ethyl sodioacetoacetate.

2 : 3 : 4-*Tribromo-6-nitroaniline*, $NO_2{\cdot}C_6HBr_3{\cdot}NH_2$, obtained by the action of alcoholic ammonia on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene at the ordinary temperature, crystallises from benzene in bright yellow, radiating needles, melts at 161°, and dissolves readily in benzene, chloroform, or acetone. 2 : 4-*Dibromo-6-nitro-*m*-phenylenediamine*, $NO_2{\cdot}C_6HBr_2(NH_2)_2$, formed by heating 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene with alcoholic ammonia in a sealed tube for 3 days at 100°, crystallises in bright yellow needles, melts at 189—190°, and is soluble in acetone, alcohol, ether, chloroform, or glacial acetic acid.

2 : 3 : 4-*Tribromo-6-nitrodiphenylamine*, $NO_2{\cdot}C_6HBr_3{\cdot}NHPh$, obtained by the action of aniline on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene, crystallises from alcohol in red prisms, melts at 138—139°, and is soluble in ether, benzene, chloroform, or acetone.

3 : 4 : 5-*Tribromo-*o*-phenylenediamine*, $C_6HBr_3(NH_2)_2$, formed by the reduction of 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene with tin and hydrochloric acid, melts at about 91°, becomes brown on exposure to the air, and is freely soluble in ether or acetone; its *hydrochloride* was prepared and analysed. By the condensation of this diamine with phenanthraquinone, *diphenylene*-3 : 4 : 5-*tribromoquinoxaline* is produced as a yellow solid which does not melt below 250°. By condensation of the diamine with benzil, *diphenyl*-3 : 4 : 5-*tribromoquinoxaline* is obtained, which forms a light, brick-red powder and dissolves readily in benzene or chloroform. E. G.

m-Nitronitrosobenzene. FREDERICK J. ALWAY (*Ber.*, 1903, 36, 2530—2531).—m-*Nitronitrosobenzene*, $NO{\cdot}C_6H_4{\cdot}NO_2$, prepared by reducing *m*-dinitrobenzene to the hydroxylamino-compound and oxidising, crystallises from alcohol in a white or bluish-green powder and melts at 85° (corr.); it condenses with aniline to *m*-nitroazobenzene.

T. M. L.

So-called Styrene Nitrosites. Preparation of Hyponitrous Acid. HEINRICH WIELAND (*Ber.*, 1903, 36, 2558—2567).—Styrene pseudonitrosite, Sommer's α-styrene nitrosite (Abstr., 1895, i, 456; 1896, i, 294) is best obtained by passing nitrous gases from white arsenic and nitric acid of sp. gr. 1·38 into a well-cooled ethereal solution of styrene until the solution has a light green colour. The mixture is kept for two hours and the crystals then removed. It melts and decomposes at 129° and not at 158°, and is decomposed when boiled with any of the ordinary solvents. Boiling with water or alcohol largely transforms it into Sommer's β-styrene nitrosite, which is now shown to be α-nitroacetophenone oxime, $OH{\cdot}N{:}CPh{\cdot}CH_2{\cdot}NO_2$. When boiled with concentrated hydrochloric acid, the oxime yields a considerable amount of benzonitrile and benzoic acid. Styrene pseudonitrosite has the double molecular formula, and is undoubtedly a nitrobisnitroso-compound, $N_2O_2{\cdot}(CHPh{\cdot}CH_2{\cdot}NO_2)_2$, and its conversion into α-nitroacetophenone oxime is exactly analogous to the conversion of bisnitrosylbenzyl into benzaldoxime (Behrend and König, Abstr., 1890, 1132).

Aniline converts the pseudonitrosite into a base,

$NO_2\cdot CH_2\cdot CHPh\cdot NHPh$,

and nitrous oxide. Piperidine and phenylhydrazine behave in a similar manner.

Sodium hydroxide reacts with the pseudonitrosite yielding benzaldehyde, nitromethane, hyponitrous acid, and a small amount of nitrous oxide. Sodium ethoxide reacts in a similar manner; the hyponitrous acid has been obtained in the form of its silver salt, which is not explosive (compare Divers, Proc., 1899, 14, 223). The formation of the hyponitrous acid is due to the elimination of the bisnitroso-group by the metal and the production of the sodium salt of phenylnitroethanol ether, $OEt\cdot CHPh\cdot CH{:}NO_2Na$, which further decomposes into benzaldehyde and sodionitromethane. J. J. S.

9-Nitrophenanthrene and its Reduction Products (Studies in the Phenanthrene Series. VI). Julius Schmidt and Max Strobel (*Ber.*, 1903, 36, 2508—2518).—9-*Nitrophenanthrene* has already been prepared by Schmidt (Abstr., 1901, i, 76) from sodium methoxide and nitrobisdihydrophenanthrene oxide. A more convenient method is to nitrate phenanthrene dissolved in glacial acetic acid in presence of acetic anhydride (compare Pictet and Genequand, Abstr., 1902, i, 584). The product, when crystallised from alcohol, melted at 116—117°, and was further identified by its conversion into 9-amino- and 9-hydroxy-phenanthrenes and by its oxidation with chromic acid. The *picrate* softens at 96° and melts at 98—99°.

9-*Azoxyphenanthrene*, $ON_2(C_{14}H_9)_2$, crystallising with $1C_2H_6O$, is prepared by the electrolytic reduction of 9-nitrophenanthrene in hot alcoholic alkaline solution. It forms minute, bordeaux-red needles which melt and decompose at 254—255°; when dissolved in cold concentrated sulphuric acid, it exhibits an intensely blue colour. When 9-nitrophenanthrene is reduced by zinc dust and potassium hydroxide solution in presence of alcohol, 9-*azophenanthrene* is produced in small quantity. It crystallises in coloured needles, begins to decompose at 270°, and does not completely melt at 320°. It also gives, with concentrated sulphuric acid, a blue coloration with a tinge of red.

9-Azoxyphenanthrene and 9-azophenanthrene are the first representatives of their kind in the phenanthrene series.

When 9-nitrophenanthrene is reduced with zinc dust and alcoholic ammonia, 9-aminophenanthrene is generally formed. In some experiments, however, a product melting and decomposing at 220—221° was isolated, and was probably 9-hydrazophenanthrene.

9-*Aminophenanthrene* has been previously described (Schmidt and Strobel, Abstr., 1901, i, 464. Compare Japp and Findlay, Trans., 1897, 71, 1123). Its *sulphate* crystallises in needles of a silvery lustre and melts at about 230°; the *nitrate* forms white needles melting and decomposing at 163°; the *oxalate* forms yellowish-white needles melting and decomposing at 215°. Its *monobenzenesulphonyl* derivative, $C_{14}H_9NH\cdot SO_2Ph$, crystallises from alcohol in glistening, white needles which melt at 194—195°. The *dibenzenesulphonyl* derivative, formed

as a bye-product from the preceding preparation, crystallises from alcohol in white needles which melt at 263—264°.

s-*Di-9-phenanthrylthiocarbamide*, $S{:}C{:}(NHC_{14}H_9)_2$, prepared from 9-aminophenanthrene, alcohol, and carbon disulphide, separates in quadratic prisms and pyramids melting at 229°.

9-*Dimethylaminophenanthrene methiodide*, prepared from a methyl alcoholic solution of 9-aminophenanthrene and methyl iodide in presence of sodium methoxide, forms transparent, brown prisms which melt and decompose at 217°.

When 9-aminophenanthrene is diazotised, bye-products, consisting mainly of 9-azoxy- and 9-azo-phenanthrenes, are formed. The diazonium compound yields the known 9-hydroxyphenanthrene melting at 149°, which was further identified by conversion into its acetyl derivative melting at 77°. By the action of diazophenanthrene sulphate on an alkaline solution of β-naphthol, 9-*phenanthreneazo-β-naphthol* is produced; it forms dark reddish-brown crystals which soften at 200° and melt completely at about 240°. A. McK.

New Formation of Diphenylamine Derivatives. FRITZ ULLMANN (*Ber.*, 1903, 36, 2382—2384).—When *o*-chlorobenzoic acid is heated with aniline and copper powder, condensation takes place, and phenylanthranilic acid, $NHPh{\cdot}C_6H_4{\cdot}CO_2H$, is formed. The presence of copper is necessary to the reaction, which may also be extended to other aromatic amines.

m-Nitrophenylanthranilic acid, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, from *m*-nitroaniline and *o*-chlorobenzoic acid, forms yellow needles melting at 215°, insoluble in water, but dissolving readily in alcohol.

C. H. D.

Diphenyldimethylammonium Salts. S. GADOMSKA and HERMAN DECKER (*Ber.*, 1903, 36, 2487—2489).—It was formerly generally supposed that the existence of quaternary diphenylammonium salts was improbable, since no additive product could be prepared from alkyl haloids and methyldiphenylamine. When, however, molecular quantities of methyl sulphate and methyldiphenylamine are heated for two hours at 140—150°, the main product is *diphenyldimethylammonium methyl sulphate*, which forms deliquescent, colourless crystals with all the characteristics of true quaternary salts. On treatment first with water and then with a saturated aqueous solution of potassium iodide it is converted into *diphenyldimethylammonium iodide*, colourless needles which melt at 163° and, at a higher temperature, decompose to form methyl iodide and methyldiphenylamine. A. McK.

Molecular Rearrangement of Iminoacid Anhydrides. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1903, 30, 24—39).—The experiments described in this paper were undertaken with the object of investigating the formation and properties of some iminoacid anhydrides of the type of the hypothetical iminoformic anhydride, $NH{:}CH{\cdot}O{\cdot}CH{:}O$. It was expected that such compounds would

undergo a molecular rearrangement into diacylamides of the type $CHO\cdot NH\cdot CHO$, and similarly that derivatives of di-iminoformic anhydride would be transformed into acylamidines,

$$NH{:}CH\cdot O\cdot CH{:}NH \longrightarrow CHO\cdot NH\cdot CH{:}NH.$$

By the interaction of phenyl-α-chlorobenzylideneamine with silver *p*-bromobenzoate, p-*bromobenzoylbenzanilide*, $NPhBz\cdot CO\cdot C_6H_4Br$, is produced, which crystallises in colourless prisms, melts at 150°, and is readily soluble in hot alcohol or benzene. The same compound is obtained when α-chloro-*p*-bromobenzylideneaniline is treated with silver benzoate. It follows, therefore, that the iminoacid anhydrides first formed in these reactions undergo a molecular rearrangement in the cold.

p-*Bromobenzanilidimide chloride* [*α-chloro*-p-*bromobenzylideneaniline*], $C_6H_4Br\cdot CCl{:}NPh$, prepared by the action of phosphorus pentachloride on *p*-bromobenzanilide, crystallises in needles, melts at about 78°, boils at 205—207° under 12 mm. pressure, and is readily soluble in benzene or light petroleum.

When α-chlorobenzylideneaniline is treated with silver acetate, acetylbenzanilide is produced. By the action of silver benzoate on ethyl phenyliminochloroformate or of ethyl chlorocarbonate on phenyliminoethyl benzoate, *benzoylphenylurethane*, $NPhBz\cdot CO_2Et$, is formed, which crystallises in prisms and melts at 67°.

When a mixture of α-chlorobenzylideneaniline and silver anisate is suspended in dry ether and left for 16 hours, anisic anhydride is produced, together with *benzoylanisanilide*, which crystallises in six-sided tablets, melts at 162—163°, and is very soluble in alcohol or benzene; the latter substance can also be prepared by the action of anisyl chloride on phenyliminoethyl benzoate. If a mixture of α-chlorobenzylideneaniline and silver anisate is boiled with ether for $2\frac{1}{2}$ hours, benzoyldiphenylbenzenylamidine (Lander, Trans., 1902, 81, 594) is produced.

α-Chloroanisylideneaniline, $MeO\cdot C_6H_4\cdot CCl{:}NPh$, distils and decomposes at 220—230° under 17 mm. pressure, crystallises from petroleum in colourless prisms, melts at 70°, and by the action of water is converted into anisanilide

By the action of silver *m*-nitrobenzoate on α-chlorobenzylideneaniline, m-*nitrobenzoylbenzanilide*, $PhBzN\cdot CO\cdot C_6H_4\cdot NO_2$, is obtained, which crystallises in colourless prisms and melts at 139°.

By the action of acetyl chloride on the silver salt of phenylurazole, Acree (Abstr., 1902, i, 242) obtained 3-acetyl-1-phenylurazole. On repeating this experiment, it was found that a labile *diacetylphenylurazole*, $\begin{matrix}NPh\text{——}N\\ |\\ C(OAc){:}N\end{matrix}\!\!>\!C\cdot OAc$, is produced, which is very soluble in benzene; it melts at 115° and is thereby converted into the stable form, $\begin{matrix}NPh\cdot NAc\\ |\\ CO\text{--}NAc\end{matrix}\!\!>\!CO$, which melts at 162°, and is identical with the diacetyl derivative obtained by Thiele and Schleussner (Abstr., 1897, i, 380). When silver phenylurazole is treated with ethyl iodide, ethoxyphenylurazole (Acree, *loc. cit.*) is not produced, but phenylurazole is obtained together with 1-*phenyl*-3 : 5-*diethylurazole*,

$\overset{\displaystyle NPh—N}{\underset{\displaystyle C(OEt):N}{|}}\!\!>$C·OEt, which crystallises in colourless needles and melts at 46—47°. E. G.

Derivatives of Dipeptides and their Behaviour towards Pancreas Ferments. EMIL FISCHER and PETER BERGELL (*Ber.*, 1903, 36, 2592—2608).—*β-Naphthalenesulphoglycyl*-d-*alanine*,

$C_{10}H_7·SO_2·NH·CH_2·CO·NH·CHMe·CO_2H$,

prepared in the manner already described (this vol., i, 467) from naphthalenesulphoglycine, thionyl chloride and *d*-alanine ethyl ester, crystallises from water in tiny needles or glistening plates, melts at 154—155° (corr.) and in alkaline solution has $[\alpha]_D + 7·11°$. It is soluble in 50 parts of boiling water and in about 2012 parts at 20°; it forms easily soluble calcium and barium salts and amorphous, sparingly soluble silver and lead compounds.

β-Naphthalenesulpho-d-*alanylglycine*,

$C_{10}H_7·SO_2·NH·CHMe·CO·NH·CH_2·CO_2H$,

crystallises in glistening plates, melts at 180·5—181·5° (corr.) and in alkaline solution has $[\alpha]_D - 63·71°$; it is soluble in 50 parts of boiling or about 711 parts of water at 20°. The silver and lead salts are sparingly soluble, as also are the calcium and barium compounds, which crystallise in needles grouped in stellate aggregates. The *ethyl* ester crystallises in long needles from dilute alcohol and melts at 103°. The difference in solubility of the calcium and barium salts of these two acids facilitates their separation. They are of interest, as by the successive hydrolysis of silk-fibroin with hydrochloric acid, trypsin, and barium hydroxide, a product is formed, which appears to be a compound of glycine and alanine. It is, however, not identical with either of the acids described above, although possibly a mixture of the two.

β-Naphthalenesulphoglycyltyrosine,

$C_{10}H_7·SO_2·NH·CH_2·CO·NH·CH(CO_2H)·CH_2·C_6H_4·OH$,

crystallises from dilute alcohol in needles, sinters at 157—158°, melts at 163—163·5°, has $[\alpha]_D + 17·9°$ at 20° in alkaline solution and is very sparingly soluble in water. With Millon's reagent it gives a faintly red precipitate, the solution itself remaining colourless.

β-Naphthalenesulphoglycyl-dl-*leucine*,

$C_{10}H_7·SO_2·NH·CH_2·CO·NH·CH(CO_2H)·CH_2·CHMe_2$,

crystallises from 20 per cent. alcohol in long needles, melts sharply at 123—123·7° and is very sparingly soluble in water.

The analogous *l*-leucine compound was not obtained quite pure. It melts at 144—145° and has $[\alpha]_D$ about + 13°.

Carbethoxyglycyl-dl-*leucine*,

$CO_2Et·NH·CH_2·CO·NH·CH(CO_2H)·CH_2·CHMe_2$,

crystallises in plates from acetone or in needles from alcohol and water, melts at 134—135° and is soluble in 9 parts of boiling and about 100 parts of cold water.

Carbethoxyglycyltyrosine was only obtained as a syrup.

The *sodium* salt of *di-β-naphthalenesulphotyrosine*,

$C_{10}H_7·SO_2·O·C_6H_4·CH_2·CH(CO_2H)·NH·SO_2·C_{10}H_7$,

obtained on shaking an alkaline solution of tyrosine with β-naphthalenesulphonic chloride, crystallises in long needles from methyl alcohol, sinters at 250°, and melts at 252—254°. The acid crystallises from alcohol in rosettes of fine needles and on heating forms an oil at 100°, which becomes liquid at 120° and froths at 145—150° without decomposing. The ammonium and barium salts are sparingly soluble and crystallise in needles.

Di-β-naphthalenesulphotyrosyl-dl-*leucine*, formed by the interaction of the sodium salt just described with thionyl chloride and leucine ethyl ester, forms stellate aggregates of small needles, sinters at 90° and melts at 100—105°.

In the tryptic digestion of albumins, tyrosine and leucine are always the first products formed, in fact, in the case of the digestion of the peptone from silk-fibroin, their presence can be detected in 15 minutes. Similar observations have been made with the synthetic derivatives of dipeptides. These were brought into solution with a little ammonia if necessary, and digested at 37° with pancreatin in presence of toluene. Under these conditions, the glycine derivatives, namely, glycylglycine, naphthalenesulpho-*d*-alanylglycine, and naphthalenesulphoglycyl-*d*-alanine, as also hippuric acid, were not affected, whereas naphthalenesulphoglycyl-*l*-tyrosine was hydrolysed to naphthalenesulphoglycine and *l*-tyrosine almost completely in the space of 13 hours. Especially interesting results were obtained with carbethoxyglycyl-*dl*-leucine, which was hydrolysed into *l*-leucine and carbethoxyglycine, the carbethoxyglycyl-*d*-leucine remaining unattacked. E. F. A.

Oxide from β-*cyclo*Hexane-1 : 2-diol and its Derivatives. LÉON BRUNEL (*Compt. rend.*, 1903, **137**, 62—64. Compare this vol., i, 338).—An oxide is formed under various circumstances from hexahydrobenzene monoiodohydrin, $C_6H_{10}I{\cdot}OH$. For its preparation, the hydrin is dissolved in dry ether and the solution is shaken with powdered potassium hydroxide. On fractionation of the product, a small quantity of *cyclo*hexane is obtained at 83—85°, and the portion boiling at 131—132° is the pure *oxide*, $C_6H_{10}{\colon}O$. This internal oxide of β-*cyclo*hexane-1 : 2-diol is a colourless, mobile liquid with a strong odour and a burning taste; it has a sp. gr. 0·975 at 15°, does not solidify at − 10°, and is insoluble in water, but readily soluble in alcohol, ether, acetone, or acetic acid. The vapour density corresponds with the simple formula $C_6H_{10}{\colon}O$.

Reduction of the oxide with sodium amalgam gave no satisfactory result, but when hydrogen charged with its vapour was conducted over reduced nickel at 170—180°, reduction to *cyclo*hexanol, $C_6H_{11}{\cdot}OH$, takes place almost quantitatively.

The oxide can be easily hydrated; the action commences at 80° and is rapid at 110—115°, β-*cyclo*hexane-1 : 2-diol being formed.

When the oxide is agitated with a solution of sodium hydrogen sulphite, *sodium* β-cyclo*hexan*-1-*ol*-2-*sulphonate*, $OH{\cdot}C_6H_{10}{\cdot}SO_3Na$, is formed. The action takes place more readily at a higher temperature, and the salt is best prepared in a sealed tube at 110—115°. When crystal-

lised from water it separates with H_2O, which it loses at 100°; it is sparingly soluble in water and almost insoluble in alcohol. J. McC.

Attempts at an Asymmetric Synthesis. EMIL FISCHER and MAX SLIMMER (*Ber.*, 1903, 36, 2575—2587).—Most of the results described have been published previously (compare Abstr., 1902, i, 621). Gluco-*o*-hydroxyphenylethylcarbinol (*loc. cit.*), when hydrolysed with 1—3 per cent. sulphuric acid and extracted with ether, yields a syrup having $[\alpha]_D$ − 10° to − 15° at 20°, from which, on distillation under 0·3 mm. pressure, a colourless oil having $[\alpha]_D$ − 9·83° at 20° was obtained. This was at first believed to be active *o-hydroxyphenylethylcarbinol.* However, hydrolysis of the glucoside with emulsin yielded an inactive carbinol, and on careful fractionation of the active carbinol under 0·3 mm. pressure an optically active, less volatile fraction was obtained, together with the inactive carbinol. Apparently a condensation product, soluble in ether, is formed even by the dilute acid acting on the glucoside, which distils along with the carbinol and thus imparts to it the apparent optical activity. E. F. A.

Nitrosobenzoates. FREDERICK J. ALWAY and ARTHUR B. WALKER (*Ber.*, 1903, 36, 2312—2314).—By the action of light on *o*-nitrosobenzaldehyde, Ciamician and Silber (Abstr., 1901, i, 547; 1902, i, 378, 433; this vol., i, 39) have obtained *o*-nitrosobenzoic acid, and from solutions of this aldehyde in methyl and ethyl alcohols respectively they have obtained the corresponding benzoates. The authors have prepared the latter esters and others by the action of zinc dust and acetic acid on nitrobenzoates. The hydroxyamino-compounds initially formed were directly oxidised to the mixture of azoxybenzoates and nitrosobenzoates, which are readily separable by steam distillation. *Methyl* o-*nitrosobenzoate* crystallises from glacial acetic acid in colourless needles and melts at 153°. *Ethyl* o-*nitrosobenzoate* melts at 120—121°. *Methyl* m-*nitrosobenzoate* forms white crystals and melts at 93° (corr.). *Methyl* m-*azoxybenzoate* crystallises from glacial acetic acid in orange-coloured needles and melts at 136—136·5° (corr.).

Methyl p-*nitrosobenzoate* crystallises from alcohol in yellow needles and melts at 128—129·5° (corr.). *Methyl* p-*azoxybenzoate* crystallises from alcohol in flesh-coloured needles melting at 206·5—207·5° (corr.) (compare Meyer and Dahlem, this vol., i, 448). A. McK.

Formation of Ester-acids. ROBERT KAHN (*Ber.*, 1903, 36, 2531—2534).—Controversial, in reply to Wegscheider (this vol., i, 559. Compare the following abstract). T. M. L.

Action of Alcohols on Mixed Anhydrides. ROBERT KAHN (*Ber.*, 1903, 36, 2535—2538).—3-*Acetylaminophthalic anhydride*, $C_{10}H_7O_4N$, separates from benzene in yellow crystals and melts at 181°.

Benzoic p-*nitrobenzoic anhydride*, $C_6H_5\cdot CO\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, separates from carbon disulphide in white crystals, melts at 130°, and is hydrolysed by ethyl alcohol to benzoic acid and ethyl *p*-nitrobenzoate,

the ester being derived from the stronger acid, which is also the acid in which substitution has taken place. Benzoic *iso*cuminic anhydride, $C_6H_5 \cdot CO \cdot O \cdot CO \cdot C_6H_4 \cdot CHMe_2$, in which the acids are of almost equal strength, gives a mixed product when acted on by alcohol. The isomeric *benzoic mesitylcarboxylic anhydride*, $C_6H_5 \cdot CO \cdot O \cdot CO \cdot C_6H_2Me_3$, separates from carbon disulphide in white crystals, melts at 105°, and gives benzoic acid and ethyl mesitylcarboxylate; in this case, the substituted acid is esterified, although it is probably the weaker acid.

T. M. L.

Action of Cyanogen Bromide on Benzyl Cyanide. Julius von Braun (*Ber.*, 1903, 36, 2651—2653).—Cyanogen bromide reacts with an alcoholic solution of benzyl cyanide in presence of sodium ethoxide forming a faintly red precipitate almost entirely soluble in water. The insoluble portion is diphenylmaleonitrile; on hydrolysis, it forms diphenylmaleic anhydride melting at 156°. The portion soluble in water is chiefly sodium cyanide. The original alcoholic solution yields, on evaporation, the brominated benzyl cyanide, $C_6H_5 \cdot CHBr \cdot CN$, described by Reimer (Abstr., 1881, 47).

Thus cyanogen bromide here acts as a brominating agent.

E. F. A.

A New Isomerism of Ethylene Derivatives. Emil Erlenmeyer, jun. (*Ber.*, 1903, 36, 2340—2344).—If cinnamic acid be written $\frac{C_6H_5 \quad H}{H \quad CO_2H}$, and one of the three isomeric cinnamic acids $\frac{C_6H_5 \quad H}{CO_2H \quad H}$, then in passing from the latter form into the former (stable) form, rotation of one half of the molecule must take place, and according to the direction of rotation, two intermediate configurations are possible,

$$\begin{array}{r|l} CO_2H & \\ \underline{C_6H_5} & \underline{\quad H} \\ H & \end{array} \quad \text{and} \quad \begin{array}{r|l} & H \\ C_6H_5 & \quad H \\ & CO_2H \end{array}$$

in which the molecule will be in equilibrium, but which can pass readily into the more stable configurations. These two forms may also combine to a single molecule in the same way as two oppositely active isomerides. This hypothesis suggests the existence of a larger number of isomeric ethylene derivatives than is accounted for by van't Hoff's theory.

When cinnamaldehyde is condensed with racemic *iso*-α-hydroxy-αβ-diphenylethylamine (this vol., i, 412), a single product,

$$\begin{array}{l} Ph \cdot CH \cdot OH \\ \quad\; | \\ Ph \cdot CH \cdot N \colon CH \cdot CH \colon CHPh \end{array}$$

melting at 186°, is obtained. If, on the other hand, the *l*-base be employed, the product may be separated by successive crystallisation from benzene and light petroleum into two dextrorotatory compounds giving the same figures on analysis, and melting at 189—190° and 131° respectively. The *d*-base similarly yields two lævorotatory condensation products melting at 189—190° and 131° respectively. The condensation products of the active bases with benzaldehyde, on the other hand, both melt at 137° and rotate the plane of polarisation in the same direction as the corresponding base. C. H. D.

isoCinnamic Acid. ARTHUR MICHAEL (*Ber.*, 1903, **36**, 2497—2498. Compare this vol., i, 418).—A reply to Liebermann (this vol., i, 485). A. McK.

Some Derivatives of p-Sulphocinnamic Acid. F. J. MOORE (*J. Amer. Chem. Soc.*, 1903, **25**, 622—629).—The *aniline* salt of p-sulphocinnamic acid melts at 246°; the *acid sodium* salt crystallises with $2H_2O$.

By the action of bromine on p-sulphocinnamic acid, p-*sulphodibromodihydrocinnamic acid* is produced, which crystallises with $2H_2O$ and is soluble in water at 20° to the extent of 53—57 per cent.; its *barium*, *copper*, *sodium*, and *ammonium* salts were prepared. The *aniline*, *diethylaniline*, and *dimethylaniline* salts melt at 192°, 160°, and 150° respectively. The *amide* crystallises from hot water in scales and melts at 208° (uncorr.). When silver nitrate is added to an aqueous solution of the acid sodium salt of p-sulphodibromodihydrocinnamic acid, a white precipitate is produced which rapidly changes into silver bromide; if the filtrate is evaporated in a vacuum, a crystalline *substance* is obtained, which is probably the acid sodium salt of p-sulphobromocinnamic acid.

p-Sulphocinnamic acid dissolves in warm concentrated hydrobromic acid, and, on cooling, separates in thin needles containing $3H_2O$; the ordinary form of the acid, described by Rudnew (Abstr., 1875, 76), crystallises with $5H_2O$. E. G.

Formation and Transformation of Cinnamylformic Acid [Styrylglyoxylic Acid]. EMIL ERLENMEYER, jun. (*Ber.*, 1903, **36**, 2527—2530. Compare Claisen, Abstr., 1881, 169; 1882, 520).—Styrylglyoxylic acid, $CHPh:CH\cdot CO\cdot CO_2H$, can be prepared in a crystalline form by condensing pyruvic acid and benzaldehyde with sodium hydroxide, thoroughly draining the sodium salt formed, dissolving, and acidifying; the acid crystallises with $1H_2O$ and melts at 54°, or, when anhydrous, at 57°; the dibromide decomposes at 138°, and the phenylhydrazone at 158°. On reduction, it gives Fittig's α-hydroxyphenyl*iso*crotonic acid, and not benzylpyruvic acid; the reduced acid, when boiled with dilute hydrochloric acid, gives benzoylpropionic acid. T. M. L.

Condensation of Acetylenic Esters with Alcohols. CHARLES MOUREU (*Compt. rend.*, 1903, **137**, 259—261. Compare this vol., i, 399).—When methyl phenylpropiolate is treated with sodium methoxide in methyl alcohol solution, reaction takes place, and, according to the conditions, either 1 or 2 mols. of methyl alcohol condense with the acetylenic ester. When methyl phenylpropiolate is carefully added to a solution of sodium methoxide in methyl alcohol and the mixture heated for 15 hours in a reflux apparatus, then introduced into a sealed tube and heated at 125° for 4 hours, a colourless, limpid liquid is obtained. This was poured into an excess of ice-water and at once extracted with ether and rectified under diminished pressure. In this way, *methyl αα-dimethoxydihydrocinnamate*, $CPh(OMe)_2\cdot CH_2\cdot CO_2Me$, was obtained. It is a highly refractive oil with an agreeable odour, boils

at 146—147° under 16 mm. pressure, has a sp. gr. 1·112 at 21°/0° and n_D 1·5004 at 21°. A cryoscopic determination showed that it has the simple formula $C_{12}H_{16}O_4$. The molecular refraction is in agreement with the constitution given. Ferric chloride tinges an alcoholic solution of it yellow, which slowly passes into red; this change can be attributed to the hydrolysis of the acetal function. When saponified in the cold with sodium hydroxide, it gives crystals of *sodium aa-dimethoxydihydrocinnamate* with $5H_2O$, from which the free acid is obtained in prismatic crystals by treatment with the requisite quantity of dilute sulphuric acid at 0°. At the ordinary temperature, the acid loses carbon dioxide, and at the same time an oil having an aromatic odour is formed. The latter distils at about 94° under 23 mm. pressure, and was found to be a mixture of the *dimethylacetal* of *acetophenone*, $CMePh(OMe)_2$, and *a-methoxystyrene*, $OMe \cdot CPh\colon CH_2$. When the oil is treated with acetyl chloride in presence of pyridine, methoxystyrene is obtained as an aromatic liquid, which boils at 197° (corr.), has a sp. gr. 1·0158 at 0°, n_D 1·3958 at 21°, and on hydrolysis gives acetophenone.

If methyl phenylpropiolate acts on sodium methoxide at a high temperature, there is always formed a monomethoxy-derivative, $OMe \cdot CPh\colon CH \cdot CO_2Me$, which, on saponification, gives *a-methoxycinnamic acid*, $OMe \cdot CPh\colon CH \cdot CO_2H$, which can be separated from the dimethoxy-acid by aid of its sparing solubility in ether and alcohol. The acid is obtained in microscopic crystals which decompose at 160°. J. McC.

3-Nitrophthalyl Chloride and its Action with Ammonia and with Aromatic Amines. Victor John Chambers (*J. Amer. Chem. Soc.*, 1903, 25, 601—612. Compare Bogert and Boroschek, Abstr., 1902, i, 98).—*3-Nitrophthalyl chloride*, $NO_2 \cdot C_6H_3(COCl)_2$, obtained by the action of phosphorus pentachloride on 3-nitrophthalic acid, crystallises in colourless, transparent prisms, melts at 76—77°, and is readily soluble in ether or chloroform. When a stream of dry ammonia is passed over it, 3-nitrophthalimide is produced. By the action of dilute aqueous ammonia on a solution of the chloride in chloroform, 3-nitrophthalamic acid is formed. If dry ammonia gas is led into a dry ethereal solution of the chloride, 2 : 6-*nitrocyanobenzoic acid*, $NO_2 \cdot C_6H_3(CN) \cdot CO_2H$, is obtained, which crystallises in clusters of white, slender needles, melts at 99—100°, and is converted by the action of heat into 3-nitrophthalimide. *3-Nitrophthalanilide* melts at 211—212°, the corresponding p-*toluidide* melts at 223—225°, and the m- and p-*nitroanilides* melt and decompose at 225—230° and at 197—200° respectively. E. G.

Action of the Sodium Salts of Dibasic Acids on Aniline Hydrochloride, and of Aniline on Phthalyl Chloride and Succinyl Chloride. Frederick L. Dunlap and Frederick W. Cummer (*J. Amer. Chem. Soc.*, 1903, 25, 612—621).—When dry sodium phthalate is heated with aniline hydrochloride for 6 hours in a sealed tube at 200°, phthalanil is produced, but no phthalanilide can be isolated. If a mixture of sodium succinate and aniline hydrochloride is treated in the same way, succinanilide and succinanil are formed; the higher the

temperature at which the reaction takes place, the larger is the proportion of succinanil obtained.

By the action of phthalyl chloride on an ethereal solution of aniline at the ordinary temperature, aniline hydrochloride, phthalanilide, and phthalanil are produced (compare Rogoff, Abstr., 1897, i, 470, and Kuhara and Fukui, Abstr., 1902, i, 34). When succinyl chloride reacts with an ethereal solution of aniline at the ordinary temperature, succinanilide and aniline hydrochloride are produced, but no succinanil can be isolated. E. G.

3-Aminophthalimide. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1903, 36, 2494—2497).—When 3-nitrophthalic acid is reduced by ferrous hydrate, the amino-acid is formed (Onnertz, Abstr., 1902, i, 99). When, however, the ammonium salt, obtained in the course of the preparation, is decomposed by a slight excess of glacial acetic acid, white crystals of *ammonium hydrogen 3-aminophthalate* separate which melt and decompose at 117—118°. On exposure for several hours, the mother liquor begins to darken and to fluoresce, and a yellow product (possibly 3-aminophthalic anhydride), which does not melt at 280°, is obtained. When this substance, which may also be prepared by heating ammonium hydrogen 3-aminophthalate with glacial acetic acid, is boiled with ammonia, it forms *3-aminophthalimide,* which crystallises from water in minute, yellow needles, melting at 256—257°, and forms strongly fluorescent solutions. It may also be prepared by the reduction of 3-nitrophthalimide with tin and hydrochloric acid, by treatment of 3-nitrophthalic acid with ammonium sulphide, by passing ammonia over fused 3-nitrophthalic acid, or by heating 3-nitrophthalic acid with ammonium thiocyanate at 170—180°.

3-Aminophthalimide probably exists in two tautomeric forms, the one yellow and exhibiting green fluorescence, the other colourless and exhibiting violent fluorescence. A. McK.

Phenylitaconic Acid. JOSEF HECHT (*Monatsh.*, 1903, 24, 367—374).—Stobbe and Klöppel (Abstr., 1894, i, 594) obtained a small yield of phenylitaconic acid by condensing ethyl succinate with benzaldehyde in the presence of sodium ethoxide. A convenient modification of the method is described by the author. The preparation is conducted in alcoholic solution, and by using molecular proportions of ethyl succinate and benzaldehyde it is found that the formation of an acid, melting at 203°, which was observed by Stobbe and Klöppel, is to a large degree prevented.

The *dimethyl ester*, prepared by the hydrogen chloride method, is a viscid oil which boils at 186° under 19 mm. pressure. It unites with hydrogen cyanide, and, on hydrolysis of the product, *a-phenyltricarballylic acid* is obtained; this crystallises from water in short, transparent prisms melting at 110°. A. McK.

[Formation of Carbon Rings.] ARTHUR KÖTZ (*J. pr. Chem.*, 1903, [ii], 68, 148—152. Compare Kötz and Speiss, Abstr., 1902, i, 12).—A *résumé* of the work of various authors on the formation of carbon

rings by the action of halogens and dihaloids on disodium derivatives of the esters of ethane and other tetracarboxylic acids.

The action of methylene di-iodide on ethyl disodioethanetetracarboxylate leads to the formation of ethyl *cyclo*trimethylenetetracarboxylate. The action of *meta*- and *para*-xylyldibromides does not lead to the formation of ring compounds.

A 6 : 7 double-ring *compound*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2\cdot C(CO_2Et)_2}{CH_2\cdot C(CO_2Et)_2}>CH_2$, is formed by the action of *o*-xylyl dibromide on ethyl disodiopropanetetracarboxylate. G. Y.

Action of Hydrated Bismuth Oxide on Isomerides of Gallic Acid. Bismutho-pyrogallolcarboxylic Acid. PAUL THIBAULT (*Bull. Soc. chim.*, 1903, [ii], 29, 680—682. Compare Abstr., 1902, i, 101, 240, and this vol., i, 633).—*Bismutho-pyrogallolcarboxylic acid*, prepared by the long-continued action of gelatinous bismuth oxide on pyrogallolcarboxylic acid in closed vessels at the ordinary temperature, crystallises in golden-yellow, prismatic needles, decomposes at 195—200°, and has sp. gr. 3·51 at 18°. An aqueous solution of ferric chloride at first colours the acid blue, and finally dissolves it, forming a colourless liquid. The *ammonium* and *sodium* salts are crystalline; the anilide could not be prepared. When pyrogallolcarboxylic acid is digested with hydrated bismuth oxide at 100°, there is formed a brown powder of the composition $C_6H_3O_6Bi_3,2H_2O$, which is partially soluble in sodium hydroxide solution. Phloroglucinolcarboxylic acid does not react at the ordinary temperature with hydrated bismuth oxide, but at 100° a brick-red powder of the composition $C_6H_3O_6Bi_3$ is produced. T. A. H.

Constitution of α-Oxylactones. EMIL ERLENMEYER, jun. (*Ber.*, 1903, 36, 2344—2348).—The α-oxylactones may be formulated either as ketonic or enolic compounds:

$$\text{I.}\quad \begin{array}{l} R\cdot CH\text{——}CHR' \\ \quad | \qquad\quad | \\ \quad CO\cdot CO\cdot O \end{array} \qquad \text{II.}\quad \begin{array}{l} R\cdot C\text{——}CHR' \\ \quad \| \qquad\quad | \\ HO\cdot C\cdot CO\cdot O \end{array}.$$

The first formula contains two asymmetric carbon atoms, and two racemic modifications are therefore possible. The second contains only one asymmetric carbon atom and a double linking, and, a closed ring being present, only one pair of optically active modifications is possible. The discovery of geometrical isomerides of α-oxylactones would therefore be evidence for the keto-formula (compare Abstr., 1902, i, 543).

The condensation of piperonal with phenylpyruvic acid yields two *α-oxylactones* of the formula $CO<\genfrac{}{}{0pt}{}{CHPh}{CO-O}>CH\cdot C_6H_3\colon O_2\colon CH_2$, which may be separated by their different solubility in alcohol. The more soluble lactone melts at 208°, its *acetyl* derivative at 135°, and its *benzoyl* derivative at 177°, the less soluble form melts at 205°, and its *acetyl* and *benzoyl* derivatives at 130° and 172° respectively. The acetyl and benzoyl derivatives of the two lactones are thus not identical, and must therefore also be derived from the ketonic form,

$\begin{array}{l}R\cdot CO\cdot CR'\text{—}CH\cdot R'' \\ \quad\;\; | \qquad\qquad | \\ \quad CO\cdot CO\cdot O\end{array}$. Reduction of the α-oxylactones, melting at 208° and 205°, yields *α-hydroxylactones* melting at 155° and 153° respectively.

The α-oxylactones obtained from cuminaldehyde and phenylpyruvic acid (this vol., i, 419) behave similarly. The *acetyl* and *benzoyl* derivatives of the lactone melting at 186° melt at 120° and 140° respectively, while the lactone melting at 198° forms an *acetyl* derivative melting at 156° and a *benzoyl* derivative melting at 126°. C. H. D.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XI. Behaviour of Acid-esters of Hemipinic Acid towards Hydrazine Hydrate and Thionylchloride. RUDOLF WEGSCHEIDER and PETER VON RUŠNOV (*Monatsh.*, 1903, 24, 375—390).—*Hemipinicdihydrazide*, $C_6H_2(OMe)_2\cdot(CO\cdot NH\cdot NH_2)_2$, formed by boiling α-methyl hydrogen hemipinate with hydrazine hydrate, melts in a closed capillary tube at 215°, and is partially decomposed by heating with water or with ether. When repeatedly crystallised from alcohol, it forms *hemipinichydrazide*, $C_6H_2(OMe)_2<\begin{array}{l}CO\cdot NH \\ CO\cdot NH\end{array}$, which melts at 218—221° on being slowly heated in a closed capillary tube. When strongly heated, methylamine is evolved, the dihydrazide behaving similarly. At the laboratory temperature, α-methyl hydrogen hemipinate interacts with hydrazine hydrate to form the hydrazine salt, a trace of dihydrazide being also produced.

The behaviour of *b*-methyl hydrogen hemipinate towards hydrazine hydrate is similar. In both cases, therefore, hydrazine hydrate interacts not only with the CO_2Me group but also with the carboxyl group. Hemipinic anhydride is formed by the action of thionyl chloride on *b*-methyl hydrogen hemipinate. The ester chloride, owing to its instability, could not be isolated; it undergoes considerable transformation into the isomeric α-chloride. By the action of ammonia on a mixture of thionyl chloride and *b*-methyl hydrogen hemipinate, no amide formation was observed, but *a*- and *b*-methyl hydrogen hemipinates were respectively isolated and were identified by their melting points and by determinations of their electrical conductivities. A similar transformation of *b*-acid-ester into the *a*-isomeride by means of a solution of hydrogen chloride in methyl alcohol has been previously noted by Wegscheider (Abstr., 1895, i, 420), the reaction proceeding slowly with the intermediate formation of normal ester. In the case now studied, the change was rapid and no appreciable amount of normal ester was formed. In addition to the acid-esters formed from ammonia, thionyl chloride, and *b*-methyl hydrogen hemipinate, a substance of the constitution $C_{10}H_{14}O_5N_2$ was isolated. A. McK.

Lichens and their Characteristic Constituents. VIII. OSWALD HESSE (*J. pr. Chem.*, 1903, [ii], 68, 1—71. Compare Abstr., 1902, i, 680).—The author claims to have been the first to obtain barbatic acid from *Usnea longissima* (Abstr., 1897, i, 255. Compare Zopf, Abstr., 1898, i, 89; 1902, i, 788). Barbatic acid is best characterised by its potassium salt.

Usnea ceratina, from the Black Forest, contains *d*-usnic acid, barbatic acid, and barbatin; that from Java cinchona bark contains *d*-usnic acid, usnaric acid, parellic acid, and ceratin (compare Zopf, Abstr., 1902, i, 789).

Usnea barbata (α) *florida*, from Bolivian cinchona bark, contains *d*-usnic acid, usnaric acid, plicatic acid, usnetic acid, and an *acid* which resembles usnaric acid, but is tasteless.

The author replies to Widman (Abstr., 1903, i, 96).

Usnea barbata (β) *hirta*, from Bolivian cinchona bark, contains *d*-usnic acid and barbatic acid, the latter in larger proportion.

Stenhouse and Groves's formula, $C_{19}H_{20}O_7$, for barbatic acid is confirmed. The sodium salt, $C_{19}H_{19}O_7Na,2H_2O$, crystallises when pure in glistening, straight-sided leaflets (Zopf, Abstr., 1902, i, 789). The action of acetic anhydride on barbatic acid leads to the formation of a *substance*, probably the lactone of acetylbarbatic acid, which melts at 250°, and, on recrystallisation from glacial acetic acid, yields *acetylbarbatic acid*. This crystallises in small, white needles, melts at 172°, is soluble in ether, alcohol, acetone, or aqueous alkalis or alkaline carbonates, gives a brownish-yellow coloration with ferric chloride in alcoholic solution, and forms an amorphous potassium salt. Hydrolysis of acetylbarbatic acid or of barbatic acid with aqueous alkalis leads to the formation of betorcinol and rhizoninic acid. Rhizonic acid is identical with barbatic acid (Abstr., 1899, i, 385).

Usnea barbata (γ) *dasypoga* contains alectoric acid, contrary to Zopf's statement (Abstr., 1902, i, 789). Alectoric acid is distinguished from barbatic acid by its smaller solubility in ether and by its conversion into alectorinic acid on treatment with aqueous barium hydroxide (Abstr., 1901, i, 149). Alectorinic acid, $C_{27}H_{24}O_{13},2H_2O$, has a neutral reaction, neutralises aqueous potassium hydroxide in boiling alcoholic solution, the acid crystallising out unchanged on cooling, and gives a brownish-red coloration with ferric chloride in alcoholic solution.

Evernia furfuracea (Zopf, Abstr., 1901, i, 88) contains atranorin, evernuric acid, and traces of furevernic acid. The formula of evernuric acid is now given as $C_{24}H_{26}O_9$; the *potassium* salt,

$$C_{24}H_{25}O_9K,2H_2O,$$

crystallises in short, colourless prisms. The action of barium hydroxide on the acid leads to the formation of *evernurol*, $C_{23}H_{26}O_7$, which crystallises in short, white prisms, melts at 196°, and is soluble in ether, alcohol, or hot chloroform, but less so in benzene. The alcoholic solution is neutral, and gives a greenish-brown coloration with ferric chloride and a blood-red coloration with bleaching powder. *Furevernic acid* crystallises in small, white prisms, melts and decomposes at 197°, is easily soluble in ether, alcohol, or aqueous alkalis, and dissolves in concentrated sulphuric acid to a colourless solution which gradually becomes brown.

Ramalina farinacea contains *d*-usnic acid and *ramalic acid*, $C_{30}H_{26}O_{15}$. The new acid forms small, white needles, melts and decomposes at 240—245°, has a bitter taste, and is moderately soluble in hot glacial acetic acid or alcohol. The alcoholic solution has an acid reaction and gives a purple-red coloration with ferric chloride. It dissolves in concentrated sulphuric acid to a yellow solution which becomes blood-red,

and, on addition of water, yields an orange-coloured, flocculent decom position *product.*

Cetraria islandica, from the Gerlinger Höhe, contains protocetraric acid and proto-α-lichesteric acid. The moss previously obtained from Stuttgart and Frankfurt (Abstr., 1898, i, 534) contained protocetraric acid and protolichesteric acid. Protolichesteric acid melts at 108—109° and is converted by acetic anhydride into lichesteric acid (m. p. 124°) (Sinnhold, Abstr., 1899, i, 13). Proto-α-lichesteric acid, $C_{18}H_{30}O_5$, melts at 106—107°, is converted by acetic anhydride into α-lichesteric acid, which melts at 122°, and is identical with Zopf's protolichesteric acid (Abstr., 1902, i, 788). The protolichesteric acids form very soluble ammonium salts, and their potassium salts are easily oxidised by potassium permanganate; the lichesteric acids form crystalline ammonium salts and are not easily oxidised by potassium permanganate. *Methyl proto-α-lichesterate* crystallises in glistening leaflets and melts at 33°. The action of aqueous barium hydroxide solution on the acid leads to the formation of lichestronic acid, which melts at 80° (Abstr., 1901, i, 87). β-Lichesteric acid is identical with α-lichesteric acid, as is also probably γ-lichesteric acid. Böhme's results (Abstr., 1903, i, 316) are due to his method of extraction, which ensures changes taking place in the product. From Böhme's Iceland moss, the author obtains proto-α-lichesteric acid.

Parmelia conspersa, from Wildbad, contains *d*-usnic acid and conspersaic acid, but no usnetic acid (Abstr., 1898, i, 90, 680). *Conspersaic acid* forms granular aggregates of microscopic needles, melts and decomposes at 252°, has a bitter taste, is slightly soluble in hot alcohol or acetone, and gives a purple coloration with ferric chloride in alcoholic solution. The ammoniacal solution gives a white, flocculent precipitate with barium chloride; the solution in warm aqueous potassium hydrogen carbonate, on cooling, deposits small, white needles which assume an orange-colour; on addition of water, the solution in concentrated sulphuric acid yields a red, flocculent precipitate mixed with colourless needles.

Parmelia saxatilis retiruga, from Reunbachtale (Wildbad), contains atranorin, protocetraric acid, and *saxatic acid*, $C_{25}H_{40}O_8$, which crystallises in colourless leaflets, melts at 115°, is soluble in alcohol, acetone, or ether, and dissolves in aqueous alkali carbonates to colourless solutions which become yellow on warming; the solution in concentrated sulphuric acid becomes brown on warming; the ammoniacal solution gives an amorphous precipitate with barium chloride.

Parmelia saxatilis omphalodes contains atranorin, saxatic acid, and an acid resembling protocetraric acid.

Parmelia cetrata, from Java cinchona bark, contains *cetrataic acid*, $C_{29}H_{24}O_{14}$, which crystallises in small, white, six-sided needles, melts and decomposes at 178—180°, is soluble in alcohol, less so in ether, has a bitter taste, and gives a purple coloration with ferric chloride in alcoholic solution. The solution in concentrated sulphuric acid is yellow, slowly darkening, and becoming blood-red and brown on warming.

Lecanoric acid is not contained in *Parmelia perlata*, its presence in a previous specimen (Abstr., 1901, i, 151) being due to admixture of small amounts of *P. tinctorum*, which contains lecanoric acid and

atranorin. The moss previously supposed to be *P. olivetorum* is found to be *P. tinctorum.*

Parmelia olivetorum contains atranorin, olivetorin, and olivetoric acid (Zopf, Abstr., 1901, i, 88). Olivetoric acid is considered to have the formula $C_{21}H_{26}O_7$ (Zopf, $C_{27}H_{34}O_8$). *Olivetorin* crystallises in delicate, white needles, melts at 143°, and is soluble in alcohol or warm benzene; the alcoholic solution gives, with ferric chloride, a purple-violet, with bleaching-powder a blood-red coloration.

Parmelia olivacea is now found to contain olivacein and olivaceic acid. *Olivacein*, $C_{17}H_{22}O_6,H_2O$, crystallises in red needles, melts at 156°, and is easily soluble in alcohol, acetone, ether, benzene, or glacial acetic acid, moderately so in boiling water; the alcoholic solution gives with ferric chloride a purple-violet, with bleaching-powder a blood-red coloration. *Olivaceic acid*, $C_{16}H_{19}O_5\cdot OMe$, crystallises in small leaflets, melts at 138°, and is easily soluble in ether, acetone, or alcohol; the alcoholic solution gives purple-violet and blood-red colorations with ferric chloride and bleaching powder respectively. The *potassium* salt crystallises in small, white nodules; the *barium* salt is easily soluble in water.

Gasparrinia medians is now found to contain calycin and pulvic lactone (Abstr., 1898, i, 681).

The orange-red needles, obtained by extracting *Gyalolechia epixantha* (Ach), contain calycin and pulvic lactone and melt at 228°. The following compounds of calycin and pulvic lactone have been prepared synthetically: $C_{18}H_{10}O_4,C_{18}H_{12}O_5$, melting at 216—217°; $2C_{18}H_{10}O_4,C_{18}H_{12}O_5$, melting at 211—213°; $C_{18}H_{10}O_4,2C_{18}H_{12}O_5$, melting at 226—228°.

Contrary to Zopf's statement (Abstr., 1902, i, 790), *Urceolaria scruposa* contains lecanoric acid. The distillation in steam of pannaric acid (Abstr., 1901, i, 596) leads to the formation of *pannarol*, $C_8H_8O_2$, which crystallises in small, white needles, melts at 176°, is volatile without decomposition, is easily soluble in ether, alcohol, or acetone, gives a blue coloration with ferric chloride in alcoholic solution, and, when heated with concentrated sulphuric acid, yields the steel-blue *substance*, $C_8H_6O_3,3H_2O$, which is also obtained from pannaric acid.

Pertusaria rupestris = P. communis (β) *areolata* contains areolatin, areolin, and gyrophoric acid, $C_{16}H_{14}O_7$. *Areolatin*, $C_{11}H_7O_6\cdot OMe$, crystallises in green masses of needles, melts at 270°, and is only slightly soluble in boiling alcohol, more so in hot glacial acetic acid; the alcoholic solution, on addition of ferric chloride, is dark green by transmitted, reddish-violet by reflected light. When heated with concentrated hydriodic acid, areolatin yields *areolatol*, $C_9H_8O_4,H_2O$, which crystallises in delicate, white needles, sublimes without melting at 220°, and is easily soluble in alcohol; the alcoholic solution gives a brownish-purple coloration with ferric chloride; the solution in aqueous sodium hydroxide gives a flocculent precipitate on the addition of hydrochloric acid.

Areolin crystallises in white, globular aggregates, melts at 243°, and gives a purple-red coloration with ferric chloride in alcoholic solution.

Petrusaria glomerata, from Wildbad, contains porin and porinic acid.

Porin, $C_{42}H_{67}O_9\cdot OMe$, crystallises in small, yellow leaflets, melts at 166°, is easily soluble in hot alcohol, insoluble in aqueous alkalis, and gives no coloration with ferric chloride or bleaching-powder. The mother liquor from the methoxyl determination with porin contains *porinin*, $(C_3H_6O)_n$, which crystallises in colourless needles and melts at 70—71°. *Porinic acid*, $2C_{11}H_{12}O_4,H_2O$, crystallises in microscopic needles, loses H_2O at 100°, and melts and decomposes at 218°; the alcoholic solution gives with ferric chloride a brownish-violet, with bleaching-powder a blood-red coloration. When boiled with aqueous barium hydroxide, the acid yields a *substance*, $C_{10}H_{12}O_2$, which crystallises in flat, colourless needles, melts at 58°, after drying in a desiccator at 92°, and gives a blood-red coloration with bleaching-powder, but no colour with ferric chloride.

Calycium chlorinum, from Bastei, contains vulpic acid and calycin, but no leprarin (Abstr., 1901, i, 86).

Lepraria latebrarum contains *d*-usnic acid, atranorin, hydroxyroccellic acid, lepraric acid, and talebraric acid (compare Zopf, Abstr., 1901, i, 87).

Talebraric acid crystallises in light yellow, four-sided prisms, melts and decomposes at 208°, is slightly soluble in alcohol, ether, or glacial acetic acid, and easily so in aqueous alkalis or alkaline carbonates or ammonia; the alcoholic solution gives a dark brownish-red coloration with ferric chloride. The action of concentrated sulphuric acid and water leads to the formation of *talebrarinic acid*, which forms a yellow powder or glistening needles, melts at 182°, and gives a dark green coloration with ferric chloride.

Zopf's lepraridin, leprarinin, and lepralid are the ethyl, methyl, and *n*-propyl esters of lepraric acid. The action of hydriodic acid on lepraric acid leads to the formation of *norlepraric acid*, which crystallises in small, white needles, melts at 215°, and gives a purple-red coloration with ferric chloride. G. Y.

Nitrosobenzaldehyde. FREDERICK J. ALWAY (*Ber.*, 1903, 36, 2303—2311. Compare this vol., i, 425).—p-*Hydroxylaminobenzaldehyde*, $OH\cdot NH\cdot C_6H_4\cdot CHO$, has been prepared in small yield by Kalle and Co. (D.R.-P. 89978) by the action of zinc dust and an aqueous solution of an ammonium salt on *p*-nitrobenzaldehyde. A better method is now described, in which zinc dust is added to *p*-nitrobenzaldehyde dissolved in alcohol and glacial acetic acid.

When *p*-hydroxylaminobenzaldehyde is oxidised by sulphuric acid and potassium dichromate, a mixture of *p*-nitrosobenzaldehyde and *p*-azoxybenzaldehyde is produced.

p-*Nitrobenzaldoxime*-N-p-*formylphenyl ether*,

$$NO_2\cdot C_6H_4\cdot CH{<}^{O}_{N\cdot C_6H_4\cdot CHO},$$

is prepared by adding zinc dust to a solution of *p*-nitrobenzaldehyde in glacial acetic acid or by adding a solution of *p*-nitrobenzaldehyde in sulphuric acid to an alcoholic solution of *p*-hydroxylaminobenzaldehyde.

p-*Azoxybenzaldoxime*-N-p-*formylphenyl ether*,

$$ON_2\left(C_6H_4\cdot CH{<}^{O}_{N\cdot C_6H_4\cdot CHO}\right)_2,$$

has been prepared by the electrolytic reduction of *p*-nitrobenzaldoxime-N-*p*-formylphenyl ether in sulphuric acid solution, by the action of air on *p*-hydroxylaminobenzaldehyde, by the action of zinc dust on a solution of *p*-nitrobenzaldehyde in glacial acetic acid, and by condensation of *p*-hydroxylaminobenzaldehyde (2 mols.) with *p*-azoxybenzaldehyde (1 mol.) by means of sulphuric acid. On oxidation, it yields *p*-nitrosobenzaldehyde and *p*-azoxybenzaldehyde, whilst on being boiled with dilute acids it forms *p*-azoxybenzaldehyde only.

p-Nitrosobenzaldehyde was prepared from *p*-nitrobenzaldehyde in a manner analogous to the preparation of *p*-hydroxylaminobenzaldehyde. It may also be prepared by adding zinc dust to *p*-nitrobenzyl chloride, dissolved in alcohol and glacial acetic acid.

m-*Nitrobenzaldoxime*-N-m-*formylphenyl ether* was prepared by the reduction of *m*-nitrobenzaldehyde. It melts at 189—190° and is identical with the product obtained by the electrolytic reduction of *m*-nitrobenzaldehyde. The crude reduction product, obtained from *m*-nitrobenzaldehyde and zinc dust, gave, on oxidation, *m*-nitrosobenzaldehyde.

p-*Tolueneazo*-p-*benzylidene*-p-*toluidine*,

$$C_6H_4Me{\cdot}N_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4Me,$$

prepared from *p*-nitrosobenzaldehyde, *p*-toluidine, and acetic acid, forms orange-red leaflets melting at 170—171° (corr.). By the action of nitric acid, it yields p-*tolueneazo*-p-*benzaldehyde*, $C_6H_4Me{\cdot}N_2{\cdot}C_6H_4{\cdot}CHO$, which crystallises from glacial acetic acid in red needles melting at 177·5° (corr.). A. McK.

The Addition of Hydrogen Chloride to Dibenzylideneacetone. JOHANNES THIELE and FRITZ STRAUS (*Ber.*, 1903, 36, 2375—2378. Compare Vorländer and Mumme, this vol., i, 495).—The compound of dibenzylideneacetone with hydrogen chloride, $C_{17}H_{15}OCl$, crystallises from ether or carbon disulphide in colourless leaflets which decompose on heating. It combines with bromine in chloroform solution to form a *dibromide*, $C_{17}H_{15}OClBr_2$, crystallising from a mixture of chloroform and light petroleum in groups of colourless needles which melt at 128°. Vorländer's red dihydrochloride forms the known colourless tetrabromide when treated with excess of bromine in carbon tetrachloride solution, the hydrogen chloride being eliminated.

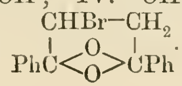
The constitution of the colourless hydrochloride must be

$$CHPhCl{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CHPh,$$

the hydrogen chloride in the dihydrochloride, on the other hand, must be differently combined, since both molecules are eliminated in contact with air or water, without intermediate formation of the monohydrochloride. C. H. D.

Chloro- and Bromo-diphenacyls. CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1903, 36, 2386—2404. Compare Abstr., 1902, i, 228).—The formulæ I—V are possible for the bromodiphenacyls:

I. $COPh{\cdot}CHBr{\cdot}CH_2{\cdot}COPh$; II. $OH{\cdot}CPh{:}CBr{\cdot}CH_2{\cdot}COPh$;
III. $COPh{\cdot}CHBr{\cdot}CH{:}CPh{\cdot}OH$; IV. $OH{\cdot}CPh{:}CBr{\cdot}CH{:}CPh{\cdot}OH$;

V. 

Of these, I is assigned to γ-bromodiphenacyl, leaving II—V for the α- and β-derivatives. α- and β-Chloro- and bromo-diphenacyls, unlike the γ-compounds, combine with acetyl chloride and bromide to form stable compounds (compare Paal and Stern, Abstr., 1902, i, 476). The compound from β-chlorodiphenacyl and acetyl bromide is identical with that from β-bromodiphenacyl and acetyl chloride, and the two halogen atoms must be attached to the same carbon atom. This excludes formulæ III and V. Assuming formula II for the β-derivatives, the enolic hydroxyl is first acetylated, and the hydrogen haloid formed is then taken up at the double linking. The formula II must be rejected for the α-derivatives, since the products from α- and β-chlorodiphenacyls and acetyl chloride are not identical. The properties of a- and β-halogendiphenacyls are best represented by the formula IV, of which four configurations are possible. This explains the existence of four iododiphenacyls (compare following abstract).

α-Chloro- and α-bromo-diphenacyls are isomorphous, and crystallise from ethyl acetate in large, rhombic tablets. β-Chloro- and β-bromodiphenacyls are also isomorphous, and form large, probably monoclinic, tablets. The following additive products are described:

	α-Chlorodiphenacyl.	β-Chlorodiphenacyl.
Acetyl chloride	Needles, m. p. 106°	Tablets, m. p. 98°
Acetyl bromide	Tablets, m. p. 104° Needles, m. p. 114° (dimorphous)	Identical with the product from β-bromodiphenacyl and acetyl chloride (*loc. cit.*), m. p. 90°.
Hydrogen chloride...	—	Needles, m. p. 164°
Hydrogen bromide...	—	Needles, m. p. 155°

	α-Bromodiphenacyl.	β-Bromodiphenacyl.
Acetyl bromide	Needles, m. p. 124°	Prisms, m. p. 103°
Hydrogen chloride...	—	Needles, m. p. 160°
Hydrogen bromide...	—	Needles, m. p. 145°

Ethyl chlorocarbonate reacts in boiling glacial acetic acid solution, forming the hydrogen chloride addition compounds.

The mother liquor from the crystallisation of α- and β-chlorodiphenacyls contains a small quantity of a *compound*, $C_{16}H_{13}O_2Cl$, crystallising from alcohol in white needles melting at 189°, isomeric with the chlorodiphenacyls, but yielding no diphenacyl on reduction. C. H. D.

Iododiphenacyls. CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1903, 36, 2405—2415).—The iododiphenacyls are prepared by the action of potassium iodide on the corresponding chloro- or bromo-diphenacyls. *α-Iododiphenacyl*, OH·CPh:CI·CH:CPh·OH, crystallises from chloroform in rosettes of tablets and from ethyl acetate in rhombic tablets, isomorphous with the α-chloro- and α-bromo-compounds, and melts at 70—90° according to the rate of heating. No additive product could be obtained with acetyl chloride, as decomposition occurred. *β-Iododiphenacyl*, prepared from β-bromodiphenacyl and potassium iodide, or mixed with tribenzoyltrimethylene, from ω-iodoacetophenone and

sodium ethoxide (compare Paal and Stern, Abstr., 1899, i, 367), crystallises from alcohol in long needles, from methyl alcohol in short prisms, and from chloroform or ethyl acetate in large crystals, isomorphous with the β-chloro- and β-bromo-compounds, and decomposes at 104—116°. γ-*Iododiphenacyl* is formed, together with some *trans*-dibenzoylethylene, by the action of potassium iodide on γ-chlorodiphenacyl, and crystallises from alcohol in white needles melting at 121°. Its solution in warm concentrated sulphuric acid, unlike that of the other isomerides, is not fluorescent. δ-*Iododiphenacyl*, prepared by the action of alcoholic ammonia or organic bases on the β-compound, crystallises from ethyl acetate in large, colourless, triclinic prisms, melting at 150—153° and decomposing shortly after.

An acetic acid solution of hydrogen chloride converts α-iododiphenacyl into an oily product. β- and δ-Iododiphenacyls, on the other hand, yield identical *additive* products, OH·CHPh·CCl·CH:CPh·OH, crystallising from anhydrous solvents in white, glistening needles, which melt and decompose at about 133—134°. C. H. D.

Cyanodiphenacyl. CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1903, 36, 2415—2416).—β-*Cyanodiphenacyl*,

OH·CPh:C(CN)·CH:CPh·OH,

prepared by heating either α- or β-bromodiphenacyl with potassium cyanide in alcoholic solution, crystallises from dilute alcohol in long, colourless needles and melts at 118°, and from ethyl acetate in large tables resembling those of β-chloro- and β-bromo-diphenacyls.

C. H. D.

Action of Silver Acetate on Halogen-diphenacyls. CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1903, 36, 2416—2424).—When β-iodo- or β-bromo-diphenacyl is heated with silver acetate in glacial acetic acid, *acetoxydiphenacyl*, COPh·CH(OAc)·CH:CPh·OH, is formed, crystallising from alcohol in white needles which melt at 98° and dissolve in concentrated sulphuric acid to a yellow solution with a brilliant green fluorescence. The same product is obtained from δ-iododiphenacyl. α-Bromodiphenacyl, on the other hand, loses water to form a *compound* with the molecular formula $C_{32}H_{24}O_4$, probably $\mathrm{OH{\cdot}CPh{:}CH{\cdot}C}\lessgtr\!\!{}^{\mathrm{O{\cdot}CPh}}_{\mathrm{CPh{\cdot}O}}\!\!\gtrless\mathrm{C{\cdot}CH{:}CPh{\cdot}OH}$ crystallising from dilute acetone in small, concentrically grouped needles, which melt when rapidly heated, undergoing isomeric change, and then again solidify, finally melting at 279°. A small quantity of this isomeride is also produced in the preparation of the compound from α-bromodiphenacyl, and crystallises from nitrobenzene or chloroform in small, white prisms melting at 279°.

Acetoxydiphenacyl is hydrolysed by heating with alcoholic potassium hydroxide, forming the *ketodiol*, COPh·CH(OH)·CH:CPh·OH, a yellow oil, exhibiting the same green fluorescence in sulphuric acid as the acetyl compound. Heating with acetic anhydride and sodium acetate converts it again into acetoxydiphenacyl. C. H. D.

Quinonoid Diketones. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1903, 137, 263—264).—The action of concentrated sulphuric acid on several diketo-compounds has been studied. Anthraquinone is fairly stable, but carbon dioxide and sulphur dioxide are evolved; alizarin is somewhat less resistant than anthraquinone; purpurin is less resistant than alizarin. Phenanthraquinone and α-naphthaquinone are both very resistant, but evolve carbon dioxide and sulphur dioxide. It is concluded that, at a definite temperature under the action of sulphuric acid, quinonoid diketones and quinone-phenols suffer fission between the carbonyl and phenyl groups; then the phenyl groups act by their CH constituents on the acid and reduce it.

From the relative powers of resistance, it is concluded that all substitution in an aromatic molecule decreases the stability. J. McC.

Synthesis of *s*-Tribenzoyl*cyclo*trimethylenes. CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1903, 36, 2425—2436).—When sodium acts on an ethereal solution of ω-iodoacetophenone, a mixture of *cis*- and *trans*-tribenzoyl*cyclo*trimethylenes is formed, the former preponderating. cis-1 : 2 : 3-*Tribenzoyl*cyclo*trimethylene* crystallises from alcohol, chloroform, or ethyl acetate in silky needles melting at 215°, sparingly soluble in ether. trans-1 : 2 : 3-*Tribenzoyl*cyclo*trimethylene* is more readily soluble in ether, insoluble in chloroform, and crystallises from ethyl acetate in small, white needles melting at 292°. Both forms are unattacked by bromine or potassium permanganate. A conversion of the *cis*- into the *trans*-form by boiling with quinoline could not be effected. Boiling with hydrazine hydrate converts both forms into 4 : 5-*benzoylmethylene*-4 : 5-*dihydro*-3 : 6-*diphenylpyridazine*,

$$CHBz<\begin{matrix}CH\cdot CPh{:}N\\ |\qquad\quad |\\ CH\cdot CPh{:}N\end{matrix},$$

crystallising from alcohol or ethyl acetate in golden-yellow needles which melt at 235° and are not attacked by oxidising agents. Hydriodic acid converts *cis*- and *trans*-tribenzoyl*cyclo*trimethylenes into 2 : 5-*diphenyl*-3-*phenacylfurfuran*, $O<\begin{matrix}CPh{:}CH\\ \quad\ \ |\\ CPh{:}C\cdot CH_2Bz\end{matrix}$, which crystallises from alcohol in long, white, glistening needles melting at 118°, and reacting with hydrazine hydrate to form a *ketazine*,

$$C_4OHPh_2\cdot CH_2\cdot CPh{:}N\cdot N{:}CPh\cdot CH_2\cdot C_4OHPh_2,$$

which crystallises from glacial acetic acid in small, yellow needles melting at 219—220°. When diphenylphenacylfurfuran is more strongly heated with hydriodic acid or warmed with phosphorus oxychloride, it loses water to form 2 : 5-*diphenyl*-α-*naphthafurfuran*, $(C_6H_5)_2C_{12}H_6O$, which crystallises from alcohol in slender, white needles melting at 120—121°, and dissolving in glacial acetic acid, ethyl acetate, chloroform or benzene to solutions having an intensely blue fluorescence. C. H. D.

Syntheses in the Camphor Group with Magnesium Powder. SIGNE M. MALMGREN (*Ber.*, 1903, 36, 2608—2642. Compare this vol., i, 103).—When α-monobromocamphor dissolved in xylene is heated with magnesium powder, it yields camphor and a compound, $C_{20}H_{28}O_2$,

melting at 192—193°, identical with Oddo's dicamphendione. In toluene solution, small quantities of dicamphor melting at 163—164° are also obtained. In ethereal solution, two reactions take place, the one giving rise to the formation of *magnesium bromocamphor*, which remains in solution, whilst the other forms *magnesium camphor* and magnesium bromide, which separate from the ether.

The solution and precipitate obtained in this manner are exceedingly reactive. Thus, if carbon dioxide is passed into the solution, it forms camphocarboxylic acid from the magnesium bromocamphor along with dicamphor and camphor from the magnesium camphor.

Alkyl haloids all bring about the formation of *dicamphor pinacone*, $C_8H_{14}<\begin{matrix}CH \qquad CH— \\ | \qquad\quad | \\ C(OH)\cdot C(OH)\end{matrix}>C_8H_{14}$, which is easily soluble in most organic solvents and crystallises in flat, prismatic needles melting at 151°.

With acetaldehyde, the magnesium camphor reacts very violently, a *secondary alcohol*, $C_8H_{14}<\begin{matrix}CH\cdot CHMe\cdot OH \\ | \\ CO\end{matrix}$, boiling at 223—226°, being formed in small quantities together with *acetylcamphor* boiling at 127° under 11 mm. pressure.

With benzaldehyde, a nearly theoretical yield of benzoylcamphor is formed.

Camphorylmethylpropylcarbinol, $C_8H_{14}<\begin{matrix}CH\cdot CMePr\cdot OH \\ | \\ CO\end{matrix}$, prepared by condensation with methyl propyl ketone, loses water very easily, forming an unsaturated compound, $C_8H_{14}<\begin{matrix}C{:}CMePr \\ | \\ CO\end{matrix}$, boiling at 253—260° under 756 mm. or at 158—163° under 10 mm. pressure.

With ethyl acetate, *dicamphorylmethylcarbinol*, $CMe(C_{10}H_{15}O)_2\cdot OH$, melting at 148—149° is formed along with acetylcamphor; this is a fairly strong acid, it develops a very marked coloration with iron chloride, and gives crystalline barium and copper salts. The *monoxime* crystallises in long, thin, colourless needles melting at 164°.

Dicamphorylethylcarbinol melts at 158—160°.

Propionylcamphor boils at 138·5° under 11 mm. pressure and develops an intense red coloration with iron chloride.

Butyrylcamphor boils at 146° under 12 mm. pressure.

Phenyldicamphorylcarbinol, obtained by condensation with benzoylchloride, crystallises from alcohol in plates or from light petroleum in tetrahedra and melts at 155—156°. E. F. A.

Action of Bromine on Pinene in Presence of Water. PAUL GENVRESSE and P. FAIVRE (*Compt. rend.*, 1903, **137**, 130—131).—The products of the action of bromine on pinene in presence of water were distilled in a current of steam. At first, some unchanged pinene passes over, then a heavy oil, from which cymene was isolated and a white, crystalline solid. The solid was proved to be pinene dibromide, $C_{10}H_{16}Br_2$, which melts at 167—168°. J. McC.

Fenchyl Derivatives. IWAN L. KONDAKOFF and JULIUS SCHINDELMEISER (*J. pr. Chem.*, 1903, [ii], **68**, 105—119. Compare Abstr., 1900, i, 604; 1902, i, 478).—Secondary fenchyl chloride is now found to melt

at 75°; it boils at 81—82° under 11 mm. and at 83—84° under 16 mm. pressure, has $[\alpha]_D$ +17°88′ and +15°39′ for p 11·79 and p 25·91 per cent. respectively, and, when acted on by concentrated alcoholic potassium hydroxide at 180°, yields fenchene, fenchyl alcohol, and traces of fenchyl ethyl ether (?); the fenchene boils at 159—161° and has $[\alpha]_D$ −9°65′; the fenchyl alcohol boils at 197—201° and has $[\alpha]_D$ −10°15′. The dichloride, obtained by the action of concentrated hydrochloric acid on fenchyl chloride, when free from the monochloride, crystallises in needles and leaflets, melts at 49—51°, and is optically inactive. The dibromide crystallises in two forms which melt at 49° and 52·5° respectively.

When acted on by alcoholic potassium hydroxide at 125°, the dichloride yields a hydrocarbon which boils at 181—184°, is optically inactive, has a sp. gr. 0·8524 at 21°/4°, and n_D 1·47713, has an odour resembling sylvestrene, gives the carvestrene reaction with acetic anhydride and sulphuric acid (Baeyer, Abstr., 1895, i, 153), and is not stable when exposed to air. With concentrated hydrobromic acid, it yields a *dibromide*, $C_{10}H_{18}Br_2$, which melts at 61—64°, at 59—60° after recrystallisation from light petroleum, is decomposed by alcohol, reacts with bromine, and is optically inactive in chloroform solution.

An attempt to prepare carvestrene by Baeyer's method from carone resulted in the formation of a mixture of hydrocarbons, which, with hydrobromic acid, yielded a mixture of bromides boiling at 85—138° under 11 mm. pressure. The action of alcoholic potassium hydroxide at 150° on the bromides led to the formation of a hydrocarbon which boils at 169—176°, is optically inactive, and yields a bromide boiling at 90—101° under 12 mm. pressure. The hydrocarbon corresponding with the less volatile part of the bromide mixture is decomposed by the alcoholic potassium hydroxide. Carvestrene, which has been considered stable, is decomposed by alkalis or acids, and has not yet been obtained in a state of purity.

Borneol and *iso*borneol yield a crystalline dibromide which boils at 139—142° under 12 mm. pressure and is optically inactive. The action of alcoholic potassium hydroxide on this dibromide leads to the formation of a hydrocarbon which boils at 173—175°, has a sp. gr. 0·843 at 20° and n_D 1·47586; the hydrocarbon obtained from another specimen boils at 174—179°, has a sp. gr. 0·844 at 20° and n_D 1·47588; both hydrocarbons are optically inactive. G. Y.

Resin from a Passion Flower. HENRI JUMELLE (*Compt. rend.*, 1903, 137, 206—208).—The bark of *Ophiocaulon Firingalavense* is covered with a green, wax-like substance, which proves, however, to be really a resin and not a wax. In chloroform, it dissolves to the extent of 92 per cent., in carbon disulphide, ether, and benzene, 83 per cent., in cold alcohol and toluene, 81 per cent., and in acetone 78 per cent. In all cases, the solution leaves on evaporation an amorphous deposit resembling that obtained from the resin of *Gardenia* by the same treatment. In hot water, it begins to soften at 65°, and between 85° and 90° it is quite pasty. The fresh resin has a sp. gr. 0·980, but

after fusion it has sp. gr. 1·014 to 1·020. The portion soluble in chloroform absorbs 34·7 per cent. of iodine. J. McC.

Glucoside Formation from Bioses. RICHARD FOERG (*Monatsh.*, 1903, 24, 357—363).—By the action of alcoholic hydrogen chloride on bioses, hydrolysis occurred and glucosides of the monoses were formed, whilst no acetals could be detected. By interaction of maltose, methyl alcohol, and dry hydrogen chloride under varying conditions, α-methylglucoside was produced. The same glucoside was also isolated from lactose and from sucrose respectively. A. McK.

A New Colouring Matter from Ox-bile. WILHELM FRANZ LOEBISCH and MAX FISCHLER (*Monatsh.*, 1903, 24, 335—350).—The product, obtained from ox-bile by extraction with alcohol, was dissolved in water, acidified with sulphuric acid, and extracted with ether. The ethereal solution was dried with calcium chloride and the ether expelled. The residue was then extracted, first with light petroleum and then with alcohol; the colouring matter, *bilipurpurin*, remained undissolved and formed dark violet, metallic scales on being crystallised from chloroform. Its solutions exhibit dichroism. The colouring matter does not melt or decompose at 330°; it is stable in air, and, when heated, decomposes, evolving an odour like that of pyridine. Its analysis accorded with the composition, $C_{32}H_{34}O_5N_4$, and the substance is considered to be the anhydride of bilirubin, $C_{32}H_{36}O_6N_4$. Crystallographic and spectroscopic determinations are quoted. Bilipurpurin dissolves in concentrated sulphuric acid to form a brilliant green solution, which gradually changes to bluish-green. Other colour reactions with acids and with alkalis are described. It was not found possible to convert bilirubin into bilipurpurin. Bilipurpurin is formed in the alcoholic extract from ox-bile even without addition of acid; its formation in the alcoholic extract requires, at the ordinary temperature, from 4 to 8 days, in the course of which, spectroscopic examination shows certain absorption bands, which indicate the formation of intermediate colouring matters. A. McK.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1903, 36, 2319—2322. Compare this vol., i, 270).—By the action of potassium hydroxide on dinitrotetramethylhæmatoxylone, 6-nitrohomoveratrole and 4 : 5 : 4′ : 5-tetramethoxyl-2 : 2′-dinitrodibenzyl were isolated. From that portion of the product which was soluble in alkali, the authors have isolated Perkin and Yates' 2-carboxy-5 : 6-dimethoxyphenoxyacetic acid, $C_{11}H_{12}O_7$ (Trans., 1902, 81, 235). The dinitro- and mononitro-compounds studied are soluble in dilute alkalis, the colour of the solutions being a reddish-violet, which disappears on dilution.

From hydroxylamine hydrochloride and β-trimethylbrazilone, a substance having the composition of an oxime has already been described (*loc. cit.*). Similarly, when hydroxylamine hydrochloride acts on nitrotrimethylbrazilone, an oxime is obtained which crystallises from alcohol in yellow needles melting at 159—162°. On treatment with

alcoholic hydrogen chloride, it yields the original nitro-compound, which crystallises from glacial acetic acid in yellow needles and melts at 222—225°. A. McK.

New Syntheses effected by means of Molecules containing a Methylene Group Associated with One or Two Negative Radicles. Action of Epichlorohydrin on the Sodium Derivatives of Acetonedicarboxylic Esters. III. ALBIN HALLER and F. MARCH (*Compt. rend.*, 1903, 137, 11—15. Compare this vol., i, 318).—By the action of epichlorohydrin on the methyl or ethyl ester of acetonedicarboxylic acid, a chloroketolactonic ester of the formula $CO_2R\cdot CH_2\cdot CO\cdot CH<{}^{-CH_2-}_{CO\cdot O}>CH\cdot CH_2Cl$ is formed. An alcoholic solution of the ethyl compound is saturated with hydrogen chloride, and after keeping for 48 hours the hydrogen chloride is removed under reduced pressure and the residue treated with water and extracted with ether. The ethereal solution yields an oil which has the formula $C_{12}H_{17}O_5Cl$, and boils at 198—199° under 17 mm. pressure. It gives no precipitate with cupric acetate, and does not form a semicarbazide: the ketonic function has, therefore, disappeared, and the complex $\cdot CO\cdot CH_2\cdot CO_2R$ has been changed. When boiled with an aqueous solution of potassium carbonate, it gives crystals the composition of which is represented by the formula $C_9H_{13}O_3Cl$. This melts at 57—58°, boils at 141—143° under 17 mm. pressure, is very soluble in ether or in alcohol, and has an odour resembling that of hydrofurfuran derivatives. It is identical with the ester obtained from δ-chloro-α-acetyl-γ-valerolactone, and is therefore *ethyl 2-chloromethyl-5-methyl-2:3-dihydrofurfuran-4-carboxylate.* The first action is to produce an ester by opening the lactone-ring; $CO_2Et\cdot CH_2\cdot CO\cdot CH(CO_2Et)\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$ is formed, and in the tautomeric enolic form loses a molecule of water and gives $\begin{matrix} CH_2\cdot CH(CH_2Cl) \\ | \\ CO_2Et\cdot C:C(CH_2\cdot CO_2Et) \end{matrix}>O$. The second compound is formed from this by the addition of a molecule of water and elimination of a molecule of carbon dioxide and one of alcohol:

$$C_{12}H_{17}O_5Cl + H_2O = CO_2 + EtOH + O<\begin{matrix} CMe{=\!=\!=}C\cdot CO_2Et \\ CH(CH_2Cl)\cdot CH_2 \end{matrix}.$$

The acid obtained from this dihydrofurfuran ester melts at 108—109°.

If the original keto-lactone is boiled with a dilute aqueous solution of potassium carbonate, carbon dioxide is evolved, and a substance having the formula $COMe\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ is formed; this is identical with the compound described by Traube and Lehmann (Abstr., 1901, i, 501).

By the action of benzenediazonium chloride at 0° on the sodium derivative of the keto-lactone, crystals of the compound

$$C_{11}H_{11}O_2N_2Cl$$

are formed which melt at 183—184°. The same compound is obtained by the action of benzenediazonium chloride on δ-chloro-α-benzoyl-γ-valerolactone, and its constitution is, therefore,

$$\begin{matrix} NHPh\cdot N:C\cdot CH_2\cdot CH\cdot CH_2Cl. \\ \quad | \qquad\qquad | \\ CO{-\!-\!-}O \end{matrix}$$

If *p*-toluenediazonium chloride is used, the compound

$$\begin{array}{l} C_6H_4Me\cdot NH\cdot N{:}\underset{|}{C}\cdot CH_2\cdot \underset{|}{C}H\cdot CH_2Cl \\ \qquad\qquad\qquad\quad CO\text{———}O \end{array}$$

is produced, which crystallises in colourless needles from hot alcohol and melts at 210°. J. McC.

Quinonoid Benzopyranol Derivatives from 3 : 5-Dimethoxybenzoylacetophenone. I. CARL BÜLOW and GUSTAV RIESS (*Ber.*, 1903, 36, 2292—2303).—The authors have previously shown (this vol., i, 101) that 3 : 5-dimethoxybenzoylacetophenone readily condenses with hydroxylamine and substituted hydrazines to form *iso*oxazoles and pyrazoles, and, in so doing, behaves partly as a ketonic and partly as an enolic compound, from which it was concluded that in the molecule of benzoylacetone the enolic group is adjacent to the phenyl and the ketonic group to the methyl (compare Bülow and Grotowsky, Abstr., 1902, i, 484; Bülow and Wagner, this vol., i, 647). When resorcinol is condensed with 3 : 5-dimethoxybenzoylacetophenone by heating in presence of glacial acetic acid, the enolic group in the molecule of the latter is next to the phenyl, since the product is 7-*oxy*-2-*phenyl*-4-(3′ : 5′)-*dimethoxyphenyl*-1 : 4-*benzopyranol*. The alternative formulation of 3 : 5-dimethoxybenzoylacetophenone, where the ketonic group is next to the phenyl, is held to be untenable, since benzoresorcinol could not be isolated from the product of the condensation. The *hydrochloride*, $C_{23}H_{18}O_4,HCl,1\frac{1}{2}H_2O$, crystallises from alcohol containing hydrogen chloride in golden leaflets. The free *base*, $O{:}C_9OH_4Ph\cdot C_6H_3(OMe)_2$, forms minute, red needles, which soften at 75° and melt at 110°. It is not dissolved in dilute sodium hydroxide solution in the cold and probably has the quinonoid structure. The *picrate* decomposes at 220° and melts completely at 240—245°. The *platinichloride* forms orange-yellow needles. 4 : 7-*Anhydro*-7-*oxy*-2-*phenyl*-4-(3′ : 5′)-*dimethoxyphenyl*-1 : 4-*benzopyranol sulphate* crystallises with $1\frac{1}{2}H_2O$ and, when dehydrated, melts at 220—230°. When 7-oxy-2-phenyl-4-(3′ : 5′)-dimethoxyphenyl-1 : 4-benzopyranol hydrochloride is reduced by zinc dust, it forms 7-*hydroxy*-2-*phenyl*-4-(3′ : 5′)-*dimethoxyphenyl*-1 : 4-*dihydropyran*, $CHPh{<}\begin{array}{l} O\text{——}C_6H_3\cdot OH \\ CH_2\cdot \overset{|}{C}H\cdot C_6H_3(OMe)_2 \end{array}$, which softens at 65° and melts completely at 110°. Its *acetyl* derivative softens at 85° and melts at 120—125°. From the benzopyranol, an oxime was prepared which softens at 50° and melts at 60—65°. By the action of potassium hydroxide on the benzopyranol hydrochloride, acetophenone, 3 : 5-dimethoxyacetophenone, resorcinol, and 3 : 5-dimethoxybenzoic acid are formed.

When sodium hydrogen sulphite is added to an alcoholic solution of a salt of the benzopyranol, the latter is decolorised, and when dilute acid is then added, the benzopyranol is precipitated. This indicates that the benzopyranol has the quinonoid structure.

A. McK.

Spacial Retardation. ZDENKO H. SKRAUP (*Monatsh.*, 1903, 24, 311—334).—The paper is largely theoretical and deals with the influence of spacial retardation in the different varieties of cinchonine,

in the molecules of which the groups, hydroxyl and vinyl, mutually retard one another.

Whilst cinchonine and *allo*cinchonine give reactions characteristic of hydroxylic substances, α- and β-*iso*cinchonines, on the other hand, do not. Just as cinchonine can be readily transformed into the isomeric cinchonicine, the three *iso*cinchonines can also be transformed into compounds similar to cinchonicine. Cinchonicine and the transformation product of *allo*cinchonine contain the keto-grouping and react with phenylhydrazine, in contradistinction to the transformation products of α- and β-*iso*cinchonines, which do not behave like ketonic substances. Hydrogen iodide gives one and the same additive product with all four bases, but the rate of formation of this product is much more rapid with cinchonine than with the others. Cinchonine readily unites with bromine, which attaches itself to carbon; *allo*cinchonine and α- and β-*iso*cinchonines, on the other hand, form perbromides, where the bromine is attached to nitrogen. Cinchonine and *allo*cinchonine are oxidised by potassium permanganate with approximately the same ease, whilst α- and β-*iso*cinchonines are attacked with some difficulty.

Eight stereoisomerides of cinchonine are theoretically possible (compare Skraup, this vol., ii, 67). The evidence for the constitution of the *iso*bases is described.

Experiments on the acetylation of cinchonine and *allo*cinchonine showed that the bases are acetylated at approximately equal rates.

α-*iso*Cinchonine, by aid of its hydrogen sulphate, was converted into the isomeric α-*iso*-ψ-cinchonicine, the *oxalate* of which crystallises with $3\frac{1}{2}H_2O$. The free base is precipitated from its hydrochloride by the addition of ammonia as an oil, which crystallises after a long time. The β-*iso*-ψ-cinchonicine was not obtained crystalline. The hydrochloride of the α-base was dissolved in absolute ethyl alcohol and mixed with an equivalent amount of alcoholic sodium ethoxide. The solution, so prepared, had $[\alpha]_D +4{\cdot}9°$, where $p = 0{\cdot}625$ and $d\ 20°/4° = 0{\cdot}7996$, whilst a similar solution of the β-base was practically inactive.

A. McK.

Alkaloids of Dicentra Formosa. Georg Heyl (*Arch. Pharm.*, 1903, **241**, 313—320).—The roots were digested with 80 per cent. alcohol containing some acetic acid and the extract freed from alcohol, mixed with excess of ammonia, and extracted with ether. After evaporating off the ether, protopine separated (the yield being 3 per cent.), and when purified by crystallising its hydrochloride, it melted at 201—202°. The remaining *alkaloids* were separated by fractional crystallisation of the mixed hydrobromides from dilute alcohol. Two were obtained in small quantity; that from the less soluble hydrobromide melted at 168·5—169°, the other at 142·5°; they have some resemblance to homochelidonine and chelidonine respectively, but appear to be different from these. Along with the first, a small quantity of a greenish-yellow *substance* crystallises; this softens and decomposes from 186° onwards, and gives a blue fluorescence in alcoholic solution; it is perhaps identical with the colouring matter isolated by Schlotterbeck and Watkins from *Stylophorum diphyllum* (Abstr., 1902, ii, 101; i, 231).

C. F. B.

Action of High Temperatures on Alkaloids when these are Fused with Carbamide. I. Narcotine and Hydrastine. HEINRICH BECKURTS and GUSTAV FRERICHS (*Arch. Pharm.*, 1903, **241**, 259—270).—Narcotine was heated over a bare flame with 2—3 times its weight of carbamide; as much as 50 grams of the alkaloid may be taken in one operation. The temperature rose to about 220°; much ammonia was evolved, and there was a smell of organic bases. The appearance of boiling was maintained for several minutes, the liquid allowed to cool somewhat, poured into cold water, and the solution extracted with ether. The product was meconin; no cotarnine could be detected. If a decidedly shorter or longer heating is given, the product is not wholly soluble in water; the insoluble part consists largely of unchanged narcotine with gnoscopine; these were separated by means of the insolubility of the latter in alcohol.

With hydrastine, the result was similar, meconin being formed.

Other alkaloids behave differently; for instance, narceine yields narceineimide, and papaverine is unchanged. The investigation is being continued.

It is noteworthy that meconin, when examined for nitrogen by the Dumas method, yield much inflammable gas; in one experiment, 0·3 gram gave 15 c.c. Its chloro- and bromo-derivatives behave similarly. C. F. B.

Sparteine. General Characters: Action of some Reducing Agents. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1903, **137**, 194—196).—Sparteine, obtained from the sulphate by adding alkali and extracting with ether, is a colourless, viscid liquid which boils at 188° (corr.) under 18·5 mm. pressure, and at 325° (corr.) in a current of dry hydrogen under 754 mm. pressure. It has a sp. gr. 1·034 at 0° and 1·0196 at 20°; $[\alpha]_D = -16·42°$ in alcoholic solution; $n_D = 1·5293$ at 19°. At 22°, 100 c.c. of water dissolve 0·304 gram, and it is easily soluble in the common organic solvents. It is readily volatile with steam. Analysis and cryoscopic determinations show that it has the formula $C_{15}H_{26}N_2$.

It is a strong base and can be exactly estimated by titration with alkali; towards litmus and phenolphthalein, it behaves as a monacidic base, and towards methyl-orange as a diacidic base. Its *platinichloride* has the formula $C_{15}H_{26}N_2,H_2PtCl_6,2H_2O$; its *picrate*,

$$C_{15}H_{26}N_2,2C_6H_3O_7N_3,$$

melts at 208°. These facts indicate that the two nitrogen atoms of sparteine are basic, and consequently that it is a diamine. From the investigations of Mills and of Bamberger it is certain that at least one of the aminic functions is tertiary, and since it does not give a nitroso-derivative or a benzoyl derivative, it must be assumed to be a ditertiary diamine. On treatment with hydriodic acid, it does not give methyl iodide, and therefore contains no methyl group attached to nitrogen. When subjected to the action of reducing agents (tin and hydrochloric acid, sodium and alcohol, sodium and amyl alcohol), it does not give any reduction products. It is not affected by permanganate. The latter observations show that it does not contain a double

linking, and it seems highly probable that it contains two, or even three, closed chains. J. McC.

Ammonium Compounds. XIV. Action of Alkalis on Oxydihydro-bases. HERMAN DECKER [and, in part, OSCAR ELIASBERG and WAÇLAW WISLOÇKI] (*Ber.*, 1903, 36, 2568—2572. Compare this vol., i, 516).—The volatile hydro-base obtained by the action of alkalis on methyl quinolinium salts is 1-methyltetrahydroquinoline (kairoline). It appears that of every 3 molecules of the carbinol base, two become oxidised to the alkylquinolone and one reduced to the alkyltetrahydroquinoline.

The tetrahydro-base is most readily purified by the aid of the picrate, which melts at 144·5° and not at 122—125° as stated by Ladenburg (Abstr., 1895, i, 480).

Kairoline methiodide crystallises in large plates melting and decomposing at 173°, and with picric acid yields 1 : 1-*dimethylquinolinium picrate* melting at 124°. A table is given of the solubility of quinoline, 1-methylquinolinium, kairoline, and 1 : 1-dimethylquinolinium picrates in water, alcohol, and benzene.

Quinoline ethiodide, when decomposed with alkalis, yields quinoline and ethyltetrahydroquinoline, the *picrate* of which melts at 117—118°.

J. J. S.

2:4-Substituted-7-hydroxyquinolines. CARL BÜLOW and GOTTHOLD ISSLER (*Ber.*, 1903, 36, 2447—2459).—In condensation reactions, *m*-aminophenol acts sometimes as a phenol and sometimes as an amino-compound. It is now found that *m*-aminophenol condenses with 1 : 3-diketones to form 7-hydroxyquinoline derivatives; the amino-group is accordingly in this case more reactive than the hydroxyl, since, if the reverse were the case, the condensation products would be benzopyranol derivatives.

Anilides are formed as intermediate products, for example,

$$OH\cdot C_6H_4\cdot NH_2 + O{:}CMe\cdot CH_2\cdot COPh = H_2O + OH\cdot C_6H_4N{:}CMe\cdot CH_2\cdot COPh;$$

the ketonic group adjacent to the methyl group reacts with the amino-group of the aminophenol. The anilides part with water to form hydroxyquinoline compounds and, in consequence, the 1 : 3-diketones behave in the keto-enolic form, benzoylacetone, for instance, acting according to the structure $OH\cdot CPh{:}CH\cdot COMe$. Further, when the phenyl group is in the para-position to the quinoline nitrogen atom, the enolic hydroxyl must be adjacent to the phenyl group.

Benzoylacetone m-*hydroxyanilide*, $OH\cdot C_6H_4\cdot N{:}CMe\cdot CH{:}CPh\cdot OH$, prepared by dissolving *m*-aminophenol in glacial acetic acid and then adding benzoylacetone, melts at 160°. When boiled with water, it is resolved into its components. Its *semicarbazone* forms colourless needles melting at 124°. When benzoylacetone *m*-hydroxyanilide is carefully added to concentrated sulphuric acid, it forms 7-*hydroxy*-4-*phenyl*-2-*methylquinoline sulphate*, from which the free *base* is isolated by the addition of sodium acetate. The base forms yellow needles melting at 262°, and, in accordance with its phenolic character, dissolves readily in dilute sodium hydroxide solution. Its *chloride*

becomes brightly yellow at 120° and decomposes at 280°; the *dichromate* forms red needles which begin to decompose at 175°; the *platinichloride* melts at 218—220°, the *picrate* at 208°. The *acid oxalate* contains $1H_2O$ and decomposes at 175°. The *ethoxy*-derivative, obtained by alkylating the base with ethyl bromide, forms quadratic needles melting at 91°. The *benzoate* melts at 144°.

4-*Phenyl*-2-*methylquinoline*, a yellowish-green fluorescent oil, boiling at 200—203° under 20 mm. pressure, was prepared by heating 7-hydroxy-4-phenyl-2-methylquinoline with zinc dust; its methiodide melts at 205°. When oxidised by potassium permanganate, the hydroxy-base is converted into 4-*phenyl*-2-*methylpyridine*-5 : 6-*dicarboxylic acid*. This accords with the regularities observed by v. Miller with the oxidation of quinoline derivatives (Abstr., 1890, 1324; 1891, 1094), the methyl group remaining intact. The *copper* salt was first isolated, and the acid prepared from it begins to evolve gas at 100°, and is totally decomposed at 150°. When heated, it is converted into 4-*phenyl*-2-*methylpyridine*, a colourless oil which boils at 280°. The *picrate* melts at 203°. A. McK.

Nitroquinolones and Nitrocarbostyrils. HERMAN DECKER and A. STAVROLOPOULOS (*J. pr. Chem.*, 1903, [ii], 68, 100—103. Compare Abstr., 1901, i, 654; 1902, i, 494).—8-Nitro-1-methyl-2-quinolone, formed by oxidation of 8-nitroquinoline methiodide (Abstr., 1903, i, 278) with potassium ferricyanide, melts at 133—134°, and not at 124—125° as formerly stated (Abstr., 1901, i, 654).

2-*Chloro*-8-*nitroquinoline*, obtained by the action of phosphorus pentachloride on nitromethylquinolone, forms clusters of sickle-shaped crystals, melts at 152°, and is easily soluble in benzene or chloroform. When boiled with hydrochloric acid, it yields the hydrochloride of 8-nitrocarbostyril.

8-Nitro-1-ethyl-2-quinolone, obtained by the action of ethyl iodide on the sodium derivative of nitrocarbostyril formed from chloronitroquinoline, melts at 87° (m. p. 92°, Abstr., 1901, i, 654).

The action of phosphorus bromide on 8-nitromethylquinolone leads to the formation of a 2 : 8-*tribromoquinoline*, which crystallises in large plates and melts at 165°. When boiled with hydrochloric acid, it yields 8-*dibromocarbostyril*, which crystallises in needles and melts at 188°.

8-*Dinitro*-1-*methyl*-2-*quinolone*, formed from 8-nitro-1-methyl-2-quinolone, separates from alcohol in small, yellow crystals and melts at 208°. Further nitration leads to the formation of 8 : 6-trinitro-1-methyl-2-quinolone, which is identical with the trinitro-compound obtained by nitration of 6-nitro-1-methyl-2-quinolone. G. Y.

Thioacridone and Selenoacridone. ALBERT EDINGER and J. C. RITSEMA (*J. pr. Chem.*, 1903, [ii], 68, 72—99. Compare Abstr., 1901, i, 753; 1902, i, 181).—5-*Ethylthiolacridol*, $C_{13}H_8N{\cdot}SEt$, prepared by treating thiolacridol and ethyl iodide with sodium ethoxide in alcoholic solution or by heating thioacridol with ethyl bromide at 90—100°, crystallises in yellow needles and melts at 65°; the *picrate* forms yellow needles and melts at 182—183°; the *platinichloride* forms brown needles.

5-o-*Nitrobenzylthiolacridol*, $C_{13}H_8N\cdot S\cdot C_7H_6\cdot NO_2$, prepared by the action of sodium ethoxide and *o*-nitrobenzyl chloride on thiolacridol in alcoholic solution, crystallises in light yellow leaflets and melts at 129—130°; the *picrate* forms yellow pyramids and melts at 190—191°; the *platinichloride* crystallises in small, yellow needles.

5-p-*Nitrobenzylthiolacridol* forms short, yellow crystals and melts at 152°; the *picrate* is a yellow, crystalline substance and melts at 204°; the *platinichloride* is a brown powder.

5-*Picrylthiolacridol*, $C_{13}H_8N\cdot S\cdot C_6H_2(NO_2)_3$, crystallises in long, red needles and melts at 233°.

5-o-p-*Dinitrobenzylthiolacridol*, $C_{13}H_8N\cdot S\cdot C_7H_5(NO_2)_2$, prepared by the action of sodium hydroxide on thiolacridol and *o-p*-dinitrobenzyl chloride in alcoholic solution, crystallises in whitish-yellow needles, melts at 290°, and is decomposed by warming with concentrated acids with formation of dinitrophenylmercaptan; the *picrate* forms yellow needles and melts and decomposes at 226°; the *platinichloride* is a yellow powder.

Acridyl sulphide (*acridylthiolacridol*), $C_{13}H_8N\cdot S\cdot C_{13}H_8N$, prepared by the action of 5-chloroacridine on thiolacridol in alcoholic solution or along with chloroacridine by the action of limited amounts of phosphorus pentachloride on thiolacridol, crystallises in long, yellow needles, melts at 267°, is soluble in chloroform, benzene, or xylene, but not in alcohol, ether, or acetone, is soluble in acids and reprecipitated on addition of alkalis, forms a *picrate* and a *platinichloride*, and is hydrolysed by alcoholic hydrochloric acid to acridone and thiolacridol.

Selenoacridone, prepared by the action of sodium hydrogen selenide or sodium selenide on 5-chloro- or bromo-acridine, crystallises in blackish-brown needles, melts at 238°, dissolves in alcohol or acetone to a reddish-violet, in alcoholic sodium hydroxide to a red solution, is soluble in chloroform or benzene, less so in light petroleum, and is insoluble in dilute acids. When boiled with alcohol, acetone, or alkalis, it is decomposed with formation of selenium and acridone.

5-*Benzylselenolacridol*, prepared by the action of sodium ethoxide and benzyl chloride on selenolacridol in alcoholic solution, crystallises in yellowish-white needles, melts at 110°, is soluble in the ordinary organic solvents, and is hydrolysed by boiling concentrated alcoholic hydrochloric acid with formation of acridone and benzyldiselenide. The *picrate*, $C_{20}H_{15}N\cdot Se\cdot C_6H_2(NO_2)_3\cdot OH$, crystallises in yellow needles and melts at 179°; the *platinichloride* forms a brown precipitate.

5-*Methylselenolacridol*, prepared by the action of methyl iodide and sodium ethoxide on selenolacridol in alcoholic solution or by heating methyl iodide with selenolacridol under pressure, crystallises in whitish-yellow needles, melts at 108°, is soluble in organic solvents, and is decomposed by acids with formation of acridone. The *picrate* crystallises in yellow needles and melts at 176°; the *platinichloride* forms a red precipitate.

5-*Picrylselenolacridol*, prepared by the action of sodium hydroxide and picryl chloride on selenolacridol in alcoholic solution, crystallises in red needles, decomposes at 198°, is soluble in xylene, benzene, chloroform, or glacial acetic acid, but almost insoluble in acetone,

alcohol, ether, or light petroleum, and is decomposed by acids. The *picrate* crystallises in yellow octahedra and melts at 166°; a platinichloride is not formed. 5-o-p-*Dinitrobenzylselenolacridol* crystallises in yellow prisms, melts at 273°, and is decomposed by concentrated acids. The *picrate* crystallises in yellow needles and melts at 218°; the *platinichloride* forms a brown powder. G. Y.

Some Reactions of the Di- and Tri-phenylmethane Groups. EDUARD VONGERICHTEN and CARL BOCK (*Zeit. Farb. Text. Chem.*, 1903, 2, 249—250).—The rosanilines, prepared from *o*-toluidine and diaminodiphenylmethane on the one hand, and aniline and diaminophenyltolylmethane on the other, are not identical. The authors find that diaminodiphenylmethane, when heated with excess of *o*-toluidine and *o*-toluidine hydrochloride, yields diaminophenyltolylmethane, but the phenyl group could not further be replaced by the tolyl to form diaminoditolylmethane. With triphenylmethane derivatives, however, complete interchange of phenyl and tolyl groups could be effected, triaminotritolylmethane giving, with a mixture of aniline and aniline hydrochloride, triaminotriphenylmethane, from which triaminotritolylmethane could be regenerated by the action of *o*-toluidine and its hydrochloride.

Diaminodiphenylmethane and diaminoditolylmethane, can, by oxidation of their acetyl derivatives, be converted into the corresponding ketones, which give diaminobenzohydrols on reduction with sodium amalgam (Wichelhaus, Abstr., 1889, 781). Those diaminobenzohydrols like tetramethyldiaminodiphenylcarbinol, when dissolved in acetic acid and then heated, become intensely coloured. When diaminodiphenylcarbinol is heated with an aqueous solution of aniline hydrochloride, the change represented by the equation $(C_6H_4NH_2)_2CHOH + PhNH_2 = (NH_2C_6H_4)_3CH + H_2O$ takes place. In a similar manner, triaminotritolylmethane is formed from diaminoditolylcarbinol and *o*-toluidine hydrochloride. There is no change when diaminodiphenylmethane is heated with a mixture of *m*-toluidine and *m*-toluidine hydrochloride. A. McK.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 68, 130—147). —A review of the reactions by which heterocyclic compounds have been obtained from the acylhydrazides and their derivatives. G. Y.

Synthesis of 4-Hydroxy-2-phenylquinazoline. BRONISLAS PAWLEWSKI (*Ber.*, 1903, 36, 2384—2385).—Pheno-*β*-phenylhydroxymetadiazine [4-hydroxy-2-phenylquinazoline] (compare Bischler and Lang, Abstr., 1895, i, 250) may be directly synthesised by heating thiobenzamide with anthranilic acid at 160—162°:

$$C_6H_4{<}{\begin{matrix}NH_2\\CO_2H\end{matrix}} + C_6H_5{\cdot}CSNH_2 = C_6H_4{<}{\begin{matrix}C(OH){:}N\\N{=\!=\!=}CPh\end{matrix}} + H_2S + H_2O.$$

The properties of the product are identical with those of Bischler and Lang's compound. C. H. D.

Pyridazine Derivatives. III. Ethyl Dimethylpyridazinecarboxylate. Carl Paal and Carl Koch (*Ber.*, 1903, 36, 2538—2539).—*Ethyl dimethylpyridazinecarboxylate*, $C_{12}H_{16}O_4N_2$, prepared by oxidising the dihydro-compound with nitrous acid, crystallises from light petroleum in long, white, feathery needles, melts at 22°, boils with slight decomposition at 200° under 22 mm. pressure, and under atmospheric pressure with considerable decomposition at 275°; it was previously prepared in an impure state by oxidation with nitric acid (Paal and Ubber, this vol., i, 290). T. M. L.

Products from the Hydrolysis of Diazo-ethers. Hans Euler (*Ber.*, 1903, 36, 2503—2508).—Diazo-ethers are considered by Bamberger (Abstr., 1895, i, 215) to be "normal" ethers on account of the rapidity with which they couple up and on account of their hydrolysis to normal diazoxides. Hantzsch, on the other hand (this vol., i, 210), considers them to be *anti*diazo-compounds, since he finds that diazo-ethers are hydrolysed to *anti*- and not to *syn*-diazoxides. The author has studied the behaviour of the products from the hydrolysis of diazo-ethers towards α- and β-naphthols, and his results are in accordance with Bamberger's contention.

From comparative experiments as to the ease with which α- and β-naphthols respectively couple with potassium *p*-bromobenzene*iso*diazoxide, it is concluded that α-naphthol is as suitable as β-naphthol for the characterisation of normal and *iso*diazoxides, although the view has been advanced that α-naphthol could not be used to distinguish between the *syn*- and the *anti*-isomerides. Whilst potassium benzene*iso*diazoxide, in the presence of hydrolytic agents and α- or β-naphthol, shows, after several hours, no trace of coloration or precipitation, the products of hydrolysis of diazobenzenemethyl ether couple up very quickly with α- or β-naphthol. When 0·2 or 1·2*N* sodium hydroxide solution is used, the action is practically instantaneous, whilst with 30 per cent. alkali, the action takes place after about two minutes. Hence the products of hydrolysis undoubtedly behave like *syn*-(normal)-diazo-compounds. When *p*-bromodiazobenzenemethyl ether is employed, the products of hydrolysis again behave towards α- and β-naphthols like normal diazoxides. A. McK.

Formazyl Dyes. Friedrich Fichter and J. Fröhlich (*Zeit. Farb. Text. Chem.*, 1903, 2, 251—253).—The formation of dyes from formazyl derivatives has been proved by Wislicenus (Abstr., 1893, i, 156) and by Fichter and Schiess (Abstr., 1900, i, 366), who prepared the three isomeric formazylbenzenesulphonic acids.

By the action of diazobenzene on a mixture of α-naphthol and benzylidinephenylhydrazone in alkaline solution, a mixture of formazylbenzene and benzeneazo-α-naphthol is formed with the former in excess. No formazyl formation was noted when β-naphthol was used.

By the action of diazobenzene on salicylaldehydephenylhydrazone, no azo-compound was formed; the *o-hydroxyformazylbenzene*,

$$OH{\cdot}C_6H_4{\cdot}C(N{:}NPh){:}N{\cdot}NHPh,$$

formed instead, separates from alcohol as a black, crystalline powder

melting at 164—165° and dissolving in alkalis to a brown solution. It was further identified by its giving, when heated with glacial acetic acid and concentrated sulphuric acid, o-*hydroxyphenyl-a-benzotriazine*, which crystallises from alcohol in yellow needles melting at 167°.

Salicylaldehydephenylhydrazone combines with diazobenzene-*p*-sulphonic acid in alkaline solution to form *potassium* o-*hydroxyformazylbenzene*-p-*sulphonate*, $OH\cdot C_6H_4\cdot C(N:N\cdot C_6H_4\cdot SO_3K):N\cdot NHPh$, which crystallises from a mixture of alcohol and chloroform in dark, glistening needles and dissolves in alkali to a yellow solution, which turns red on the addition of acid.

Piperonalphenylhydrazone in alkaline solution combines with diazobenzene to form *methylene*-3 : 4-*dioxyformazylbenzene*,

$$CH_2O_2:C_6H_3\cdot C(N:NPh):N\cdot NHPh,$$

which crystallises from alcohol in dark red needles melting at 156°. Like *o*-hydroxyformazylbenzene, it suffers the triazine decomposition, giving *methylene*-3 : 4-*dioxyphenyl-a-benzotriazine*, which crystallises from alcohol in yellow needles melting at 154°. Piperonalphenylhydrazone combines, in alkaline solution, with diazobenzene-*p*-sulphonic acid to give *potassium methylene*-3 : 4-*dioxyformazylbenzene*-p-*sulphonate*, which crystallises from aqueous alcohol in dark red leaflets and forms a red solution with water.

By the action of nitroformaldehydehydrazone on potassium diazobenzene-*p*-sulphonate, *potassium nitroformazyl*-p-*sulphonate* was obtained; this crystallises from alcohol in red leaflets melting and decomposing at 213°. Its aqueous solution is reddish-yellow. Sodium *phenyl a-naphthylformazylbenzene*-p-*sulphonate* separates from alcohol as a dark powder.

Phenyl-β-naphthylformazylbenzene crystallises from benzene in dark green needles melting at 172°.

β-Naphthylphenylformazylbenzene separates from alcohol in dark red crystals melting at 150°.

p-Chlorobenzylidenephenylhydrazone and diazobenzene gave *chloroformazylbenzene*, $C_6H_4Cl\cdot C(N:NPh):N\cdot NHPh$, which crystallises from alcohol in red needles melting at 190°.

Potassium p-*chloroformazylbenzene*-p-*sulphonate* forms red needles. *Potassium phenyl-a-naphthyl*-p-*chloroformazylbenzene*-p-*sulphonate*,

$$C_6H_4Cl\cdot C(N:N\cdot C_{10}H_6\cdot SO_3K):N\cdot NHPh,$$

dissolves in alcohol to form a violet solution, from which dark red leaflets separate. A. McK.

Preparation of Carbamide by the Oxidation of Albumin with Permanganate. ADOLF JOLLES (*Zeit. physiol. Chem.*, 1903, 38, 396—398. Compare Abstr., 1901, i, 583).—The author refers Abderhalden (this vol., i, 588) to Lanzer's results (this vol., ii, 584), which confirm his own earlier work. J. J. S.

Tryptic Fermentation of Gelatin. TH. RICHARD KRÜGER (*Zeit. physiol. Chem.*, 1903, 38, 320—322).—Trypsin-glutinpeptone-*β*, obtained by Siegfried's method, has the composition $C_{19}H_{30}O_9N_6$. Molecular weight determinations point to the doubled formula, and the compound

would then be a dibasic acid. It has $[\alpha]_D - 100·8°$ at 20°, and it usually contains minute traces of sulphur. Other peptones are formed at the same time by the action of trypsin on gelatin. J. J. S.

Sodium Phenyl. Action of Sodium on Ketones. Salomon Farby Acree (*Amer. Chem. J.*, 1903, 29, 588—609).—From his experiments with sodium phenylacetylene, Nef (Abstr., 1900, i, 20) had assumed that sodium phenyl is formed as an intermediate product by the action of sodium on bromobenzene.

Sodium phenyl, PhNa, formed when mercury diphenyl is dissolved in dry benzene or light petroleum and then acted on with sodium wire, is a light brown powder, very readily decomposable by moisture, and catches fire when exposed to the air. When ethyl bromide is gradually added to it in presence of light petroleum and the resulting product fractionated, ethylbenzene is formed as the main fraction, small amounts of benzene and ethylene being also present. Ethyl iodide behaves in an analogous manner. According to Nef's conceptions, the primary action in the latter case, for example, is the dissociation of the ethyl iodide into hydrogen iodide and alkylidene; the latter then acts on sodium phenyl to form the compound CHMePhNa, from which ethylbenzene results by the action of hydrogen iodide.

By the action of *iso*amyl iodide on sodium phenyl, benzene, *iso*amylene, and *iso*amylbenzene are formed. Benzyl chloride and sodium phenyl give diphenylmethane and stilbene. The action of sodium phenyl on bromobenzene is very vigorous, diphenyl being the main product.

Triphenylcarbinol in nearly quantitative yield is formed by the action of sodium phenyl on benzophenone. When benzoyl chloride is used, triphenylcarbinol is also produced, benzophenone being first formed and then acted on by the excess of sodium phenyl present. Sodium phenyl and benzil give a mixture of phenylbenzoin and triphenylcarbinol, which are also formed by the action of bromobenzene and sodium on benzil. Phenylbenzoin crystallises from light petroleum in radiating needles which melt at 87°. Dry carbon dioxide acts vigorously on sodium phenyl to form sodium benzoate. Sodium phenyl and ethyl chlorocarbonate give very little ethyl benzoate, since the latter acts on the excess of sodium phenyl present to form benzophenone, which then forms triphenylcarbinol.

Diphenyl-α-naphthylcarbinol is formed by interaction of benzophenone, α-bromonaphthalene, and sodium; when crystallised from ether, it melts at 135°. Diphenyl-*p*-tolylmethane, formed from benzophenone, *p*-bromotoluene, and sodium, melts at 74°.

By the action of sodium on benzophenone, a mixture of benzopinacone (m. p. 185—186°) and benzohydrol results, the latter being produced either by the action of water on the disodium compound of benzophenone or by the reduction of the benzophenone by nascent hydrogen. Benzilic acid is formed by the action of sodium and carbon dioxide on benzophenone. A. McK.

Organic Chemistry.

Propylene Derivatives. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1903, 6, 397—431. Compare Abstr., 1902, i, 417, and this vol., i, 2). —Propylene α-chloro-β-hydrin, $CH_3\cdot CH(OH)\cdot CH_2Cl$, boils at 126—127°, has a sp. gr. 1·111 at 20°, and n_D 1·43924. Potassium acetate converts it into *α-acetoxy-β-hydroxypropane*, $CH_3\cdot CH(OH)\cdot CH_2\cdot OAc$, boiling at 182—183° and having the sp. gr. 1·055 at 20° and n_D 1·4197. Hydrogen chloride converts this into the β-chloro-α-acetohydrin, $CH_3\cdot CHCl\cdot CH_2\cdot OAc$, boiling at 152—153° and having a sp. gr. 1·098 at 20°; it is hydrolysed by methyl alcohol to form propylene β-chloro-α-hydrin, $CH_3\cdot CHCl\cdot CH_2\cdot OH$, boiling at 133—134° and having a sp. gr. 1·103 at 20° and n_D 1·43623.

Nitric acid converts propylene α-chloro-β-hydrin into chloro*iso*nitrosoacetone, $CH_3\cdot CO\cdot CCl\colon NOH$, which forms brilliant crystals melting at 110° and boiling and decomposing at 180—185° (compare Glutz, *J. pr. Chem.*, 1870, [ii], 1, 142). Acetic and chloroacetic acids are formed at the same time. Chromic acid forms chloroacetone. The isomeric β-chloro-α-hydrin is oxidised by nitric acid to chloropropionic acid, and by chromic acid to acetic and formic acids.

[In the original paper, the name "propylene α-chlorohydrin" is given to the compound described above as "propylene α-chloro-β-hydrin;" this substance was called "propylene β-chlorohydrin" in the author's former papers, and conversely the name "β-chlorohydrin" is in the present communication applied to the compound formerly called "α-chlorohydrin."] C. H. D.

Hydrolysis of Organic Haloids by Insoluble Oxides in Presence of Water. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1903, 6, 441—454).—When a soluble metallic hydroxide is employed as a hydrolytic agent, the reaction is checked by the accumulation of metallic ions in the solution. If, however, the metallic salt formed is insoluble or very slightly ionised, the concentration of the metallic ions cannot exceed a certain limit. The facility with which moist silver oxide converts organic halogen compounds into alcohols is due to the insolubility of the silver haloids. The present paper contains a comparison of the hydrolytic power of the oxides of magnesium, zinc, cadmium, and mercury (the last of which forms very slightly ionised salts) towards difluoroethyl bromide, $CHF_2\cdot CH_2Br$ (this vol., i, 222). The bromide was heated with the metallic oxide and water at 139—143°, and the quantity of bromide formed determined by analysis. The extent of the hydrolysis increases slowly from magnesium to cadmium, the hydrolytic power of mercuric oxide being much greater. Yellow mercuric oxide is more active than red. Finely powdered litharge is almost as active as mercuric oxide, owing to the insolubility of lead bromide. The fluorine atoms are not attacked, except to a very slight extent when magnesia is employed. C. H. D.

Action of Carbon Monoxide on Sodium Alkyloxides alone and in the Presence of Salts of Fatty Acids. WALLACE A. BEATTY (*Amer. Chem. J.*, 1903, 30, 224—244).—Geuther and Fröhlich's synthesis of salts of fatty acids by the action of carbon monoxide on sodium alkyloxides (Abstr., 1880, 622) is supposed by Nef (Abstr., 1902, i, 6) to proceed in two stages, (1) sodium formate is produced by the action of carbon monoxide on the sodium hydroxide formed from the dissociation of the sodium alkyloxide, and (2) the sodium formate is acted on by the alkylidene molecules. The formation of alkylated fatty acids from carbon monoxide, sodium alkyloxide, and a salt of a fatty acid is, according to Nef, an alkylation phenomenon. In view of Nef's interpretations, the author has repeated some of Geuther's work.

When carefully purified carbon monoxide was passed for seven hours daily, during two weeks, over sodium *iso*amyloxide heated at 180—190°, *iso*propyl*iso*amylethyl alcohol (ϵ-methyl-β-*iso*propylhexyl alcohol), γ-hydroxyundecylenic lactone, *iso*propyl*iso*amylacetic acid (δ-methyl-α-*iso*-propylhexoic acid), amyl alcohol, and much formic and *iso*valeric acids were isolated.

The foregoing decyl alcohol and the corresponding acid were also obtained on heating molecular proportions of sodium acetate and sodium *iso*amyloxide for 56 hours in a current of carbon monoxide at 180—200°; *iso*amyl alcohol, *iso*valeric acid, and γ-hydroxyundecylenic lactone were also isolated, as well as other substances which were not definitely characterised. The formation of the decyl alcohol and γ-hydroxyundecylenic lactone is interpreted from Nef's standpoint.

γ-*Hydroxyundecylenic lactone*, $C_{11}H_{20}O_2$, was heated with concentrated sodium hydroxide solution and the solution then oxidised by potassium permanganate to trans-iso*propyl*iso*butylsuccinic acid*, $CHMe_2\cdot CH\cdot CH(CO_2H)\cdot CHPr^{\beta}\cdot CO_2H$, which crystallises from water in needles and melts at 142°; it may also be made by heating γ-hydroxyundecylenic lactone with potash-lime at 250° until the evolution of hydrogen ceases.

cis-iso*Propyl*iso*butylsuccinic acid*, synthesised from sodium *iso*butyl malonate and ethyl α-bromo*iso*valerate or from ethyl α-bromo*iso*butyl-acetate and ethyl sodiomalonate, forms crystalline needles or plates and melts at 118—119°.

By the action of aqueous ammonia, the *amino-acid*,

$$C_9H_{18}(CO\cdot NH_2)\cdot CO_2H,$$

is produced; this crystallises in fine, silky needles melting at 145—146°. The *anilino-acid* crystallises from alcohol in needles and melts at 149—150°, whilst the *toluidino-acid* melts at 156—157°.

The interconversion of the *cis*- and *trans*-*iso*propyl*iso*butylsuccinic acids was not effected. Each is recovered unaltered after being heated with concentrated hydrochloric acid at 200—250°.

When carbon monoxide was passed over sodium ethoxide and sodium acetate heated at 180—200° for 28 hours, mesitylenic acid was not identified as one of the products. Butyric acid was detected when sodium ethoxide and sodium acetate were heated in absence of carbon monoxide.

Sodium acetylide is one of the products formed when sodium methoxide is heated at a temperature ranging from 260° to 400°. A. McK.

Pinacone from Methyl *iso*Propyl Ketone. I. BEAUME (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 197—204).—The reduction of methyl *iso*propyl ketone in benzene solution by means of sodium in the presence of water yields, in addition to methyl*iso*propylcarbinol, (1) *βγδε-tetramethylhexane-γδ-diol*, $C_{10}H_{22}O_2$, solidifying in the form of plates which melt at 22° and are soluble in benzene, alcohol, or ether; it is insoluble in water and forms no hydrate; it has a sp. gr. 0·9455 at 22°/0°. (2) A small quantity of a liquid compound, probably the stereoisomeric methyl*iso*propylpinacone, which, when boiled with 20 per cent. sulphuric acid solution, is converted almost quantitatively into a *liquid*, $C_{10}H_{20}O$, boiling at 185—193° and having the sp. gr. 0·8659 at 0°/0°; this compound, which is soluble in alcohol, is probably the oxide having the constitution $O<\begin{matrix}CMe\cdot CHMe_2\\ | \\ CMe\cdot CHMe_2\end{matrix}$. T. H. P.

History of the Acetals of the Polyhydric Alcohols corresponding with the Sugars. The Conditions of Combination of Mannitol with Paraldehyde. JEAN MEUNIER (*Bull. Soc. chim.*, 1903, [iii], 29, 735—742).—Largely a summary of the history of the facts relating to the combination of aldehydes with polyhydric alcohols. The best conditions for combining paraldehyde with mannitol are described, as well as the effect on the yield of varying the proportion of the reagents and the time of interaction. W. A. D.

Difluoroacetic Acid. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1903, 6, 597—633).—Difluoroacetic acid, $CHF_2\cdot CO_2H$, is best prepared by the oxidation of difluoroethyl alcohol, $CHF_2\cdot CH_2\cdot OH$ (compare Abstr., 1902, i, 129, and this vol., i, 222), with chromic acid, the product being distilled under 20 mm. pressure from a bath of glycerol. A nearly theoretical yield is obtained. After purification by fractional crystallisation, the acid boils at 134·2° (corr.) under 766 mm. pressure and melts at 0·35°. The freezing point is modified in a remarkable manner by the addition of water, the complete freezing point curve of mixtures of difluoroacetic acid and water presenting a principal maximum at −16·8° (15·8 per cent. water corresponding with the hydrate $C_2H_2O_2F_2,H_2O$), and two secondary maxima at −24·6° and −36·05° (8·57 and 36·01 per cent. water corresponding with the hydrates $2C_2H_2O_2F_2,H_2O$ and $C_2H_2O_2F_2,3H_2O$ respectively). There are four eutectic points, at −24·7°, −24·6°, −36·3°, and −36·4° (8·03, 8·96, 34·76, and 36·18 per cent. of water respectively). The curve shows no angular inflections, being rounded at the maxima and minima. The molecular weight in dilute aqueous solution is less than normal, becomes normal at 30 per cent. acid, varies little between 36 and 50 per cent., and decreases at higher concentrations, owing to the formation of the hydrate.

Determinations of the electrical conductivity of aqueous solutions show that difluoroacetic acid is completely dissociated at v_{1024}; k is found to be 5·73.

Difluoroacetic acid is decomposed by passing through a red hot platinum tube, according to the equation $C_2H_2O_2F_2 = 2CO + 2HF$. In

a glass tube, carbon is also deposited, and silicon tetrafluoride escapes.

The salts are prepared by dissolving the corresponding oxides or carbonates in the dilute acid, and dissolve readily in water or alcohol. *Sodium difluoroacetate* crystallises in large prisms, which deliquesce in moist air. The *calcium* salt forms large, non-deliquescent prisms, the *silver* salt forms small needles, very soluble in water and soluble in ether or boiling benzene. The *lead* and *mercury* salts are also described. Difluoroacetic acid resists the action of boiling water and of cold alkali hydroxides, and is only slowly converted into glyoxylic acid by barium hydroxide at 100°. A study of the velocity of this reaction showed it to be bimolecular, the hydrolysis taking place in two stages, $C_2H_2O_2F_2 + \cdot OH = C_2HO_2F_2(OH) + F$ and $C_2HO_2F(OH) + \cdot OH = C_2HO_2(OH)_2 + F$. The acid is not reduced in the cold by sodium amalgam. Bromine at 160° forms small quantities of bromodifluoroacetic acid, the properties of which will be studied later. *Ethyl difluoroacetate*, $CHF_2\cdot CO_2Et$, is a mobile liquid having a sp. gr. 1·1800 at 17°, and boils at 99·2° (corr.). Ammonia converts it into *difluoroacetamide*, $CHF_2\cdot CO\cdot NH_2$, crystallising from boiling chloroform in needles, which melt at 50·2° and volatilise at the ordinary temperature. *Difluoroacetyl chloride* is a very volatile liquid, fuming in the air and boiling at 25°. A comparison of the boiling points of these compounds with those of the other halogen derivatives shows that the replacement of chlorine or bromine by fluorine causes a regular lowering of the boiling point. C. H. D.

Preparation of α-Methyladipic Acid. EUGENE PRJEWALSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 223—226).—The author describes the preparation of α-methyladipic acid by Bouveault's method (*Bull. Soc. chim.*, 1899, [iii], 21, 1019; Abstr., 1900, i, 171) under conditions which give a 70 per cent. yield; the acid is to be further investigated.

Ethyl 1-methyl-2-keto*cyclo*pentanecarboxylate, obtained as an intermediate product in the above method, boils at 113° under 22 mm. pressure; the boiling point given by Bouveault being 108°.

T. H. P.

Synthesis of Acids of the β-Hydroxyhydrosorbic and Sorbic Series. I. W. JAWORSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 264—276).—In Reformatsky's synthesis of sorbic acid and its homologues by the interaction of crotonaldehyde and the ethyl ester of a monobromo-acid of the acetic acid series, a new class of compounds, the hydroxyhydrosorbic acids, are formed as intermediate products.

This reaction is carried out as follows: a mixture of molecular proportions of crotonaldehyde and the bromo-ester is added in small quantities to zinc, the temperature being meanwhile kept below 10°. After about twenty hours, the temperature is allowed to rise, and the mass is left in the air until it becomes quite viscid, this point being reached on the third or fourth day. It is then dissolved in aqueous ether, and dilute sulphuric acid added to bring the zinc hydroxide into solution. The

ethyl ester of the β-hydroxyhydrosorbic acid remains as a syrup after expelling the ether. The reaction is represented by the following equations:

$CRR'Br\cdot CO_2Et + CHMe\colon CH\cdot CHO + Zn =$
$CHMe\colon CH(OZnBr)\cdot CRR'\cdot CO_2Et$;

the organo-zinc compound on treatment with water yields the products $CHMe\colon CH\cdot CH(OH)\cdot CRR'\cdot CO_2Et + ZnBr\cdot OH$.

Ethyl β-hydroxyhydrosorbate, $CHMe\colon CH\cdot CH(OH)\cdot CH_2\cdot CO_2Et$, prepared from crotonaldehyde, ethyl bromoacetate, and zinc, is obtained as a mobile liquid having a pleasant, fruity odour, and boiling at 100° under 2 mm. pressure; it is soluble in ether, alcohol, or benzene, and has the normal molecular weight in freezing benzene and boiling ether; the value of the molecular refraction agrees with that calculated on the assumption that a double linking is present. The free *acid*, $C_6H_{10}O_3$, is obtained as a very viscid oil with a characteristic tarry smell, and is readily soluble in ether or alcohol. The *barium* salt was prepared and analysed.

Either β-hydroxyhydrosorbic acid or its ethyl ester can be converted into sorbic acid by boiling with a solution of barium or sodium hydroxide. T. H. P

Synthesis of Acids of the β-Hydroxyhydrosorbic and Sorbic Acid Series. II. W. Jaworsky (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 277—284. Compare preceding abstract).—*Ethyl β-hydroxy-α-methylhydrosorbate*, $CHMe\colon CH\cdot CH(OH)\cdot CHMe\cdot CO_2Et$, obtained by the action of zinc on a mixture of crotonaldehyde and ethyl β-bromopropionate, is a colourless, volatile liquid having a pleasant fruity odour, and boiling at 110—112° under 15 mm. pressure. The *acid*, $C_7H_{12}O_3$, is obtained as an oily liquid readily soluble in alcohol or ether. The *potassium* and *barium* salts were prepared; they crystallise with $1\frac{1}{2}$ and $3\frac{1}{2}H_2O$ respectively.

When heated with sodium hydroxide solution in a sealed tube or when boiled with dilute sulphuric acid for some hours, the above hydroxy-acid loses water and yields *α-methylsorbic acid*,

$CHMe\colon CH\cdot CH\colon CMe\cdot CO_2H$,

which crystallises from water in thin needles melting at 90—92° and dissolving readily in alcohol, ether, or benzene; the *copper* and *silver* salts were analysed, and the platinum, iron, lead, manganese, zinc, barium, and sodium salts prepared.

Ethyl β-hydroxy-α-ethylhydrosorbate,

$CHMe\colon CH\cdot CH(OH)\cdot CHEt\cdot CO_2Et$,

prepared by the interaction of zinc, crotonaldehyde, and ethyl α-bromobutyrate, boils at 128—130° under 15 mm. pressure, and has an odour and solubility similar to those of its lower homologues. The free *acid*, $C_8H_{14}O_3$, is a viscid liquid with a tarry odour, and dissolves readily in ether or alcohol; the *silver* salt was prepared and analysed. On boiling this acid with dilute sulphuric acid, it is converted into *α-ethylsorbic acid*, $CHMe\colon CH\cdot CH\colon CEt\cdot CO_2H$, which separates from alcohol in long, white needles melting at 75—77°, and very soluble in alcohol or ether; the *silver* and *copper* salts were prepared and analysed. T. H. P.

Synthesis of Acids of the β-Hydroxysorbic and Sorbic Series. III. W. JAWORSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 285—292. Compare preceding abstracts).—*Ethyl β-hydroxy-aa-dimethylsorbate*, CHMe:CH·CH(OH)·CMe_2·CO_2Et, prepared by the action of zinc on a mixture of crotonaldehyde and ethyl bromo*iso*butyrate, is a volatile liquid with a pleasant fruity smell and boiling at 118—120° under 17 mm. pressure; it dissolves in the same solvents as its lower homologues. The *acid*, $C_8H_{14}O_3$, has the same odour and general properties as the lower homologues; the *potassium*, sodium, and *silver* salts were prepared and analysed, the alkali derivatives crystallising with 1 and 5 mols. of water respectively.

Attempts to remove 1 mol. of water from β-hydroxy-aa-dimethylsorbic acid in order to convert it into the corresponding dimethylsorbic acid have not been successful. T. H. P.

Action of Heat on Organic Acids. WILLIAM ŒCHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1903, 633—635).—The dehydrated acids were finely powdered and mixed with pumice, and heated in a tube above their melting points. Malonic, succinic, and pyrotartaric acids oxidise to carbon dioxide and water only; in the oxidation of mucic, fumaric, and maleic acids, the formation of carbon monoxide was also observed. C. H. D.

Reduction of Complex Esters. LOUIS BOUVEAULT and GUSTAVE BLANC (*Compt. rend.*, 1903, 137, 328—329. Compare this vol., i, 673). —The esters of some unsaturated acids, hydroxy-acids, β-ketonic acids, and dibasic acids have been reduced in alcoholic solution by sodium. Ethyl oleate gave *oleyl alcohol*, $C_{18}H_{36}O$, as a colourless liquid which boils at 207° under 13 mm. pressure; with phenylcarbimide, this alcohol gave a *phenylurethane* melting at 38°.

Ethyl β-hexylcrotonate gave the saturated alcohol *γ-methylnonanol*, C_6H_{13}·CHMe·CH_2·CH_2·OH, as a colourless liquid boiling at 114—116° under 14 mm. pressure.

Ethyl cinnamate gave phenylpropyl alcohol.

The esters of the hydroxy-acids are not reduced regularly. Ethyl phenylglycollate gave only a trace of phenylglycol. Ethyl β-hydroxy-β-methyl-β-hexylpropionate and ethyl hydroxygeraniate are decomposed in the process, and gave reduction products of the ketones of which they are derivatives.

In the reduction of mono- and di-substituted derivatives of ethyl acetoacetate, decomposition of the molecule with addition of a molecule of alcohol always takes place: Me·CO·CRR'·CO_2Et + EtOH = Me·CO_2Et + CHRR'·CO_2Et. Each of the esters thus formed then undergoes reduction separately. From ethyl *iso*butylacetoacetate and ethyl methylpropylacetoacetate, *iso*hexyl alcohol and β-methylbutyl alcohol respectively have been obtained.

The esters of dibasic acids are converted into diprimary glycols, but it is difficult to separate these from the sodium hydroxide formed because they are soluble in water and insoluble in ether. Ethyl aa-dimethylsuccinate gives *β-dimethylbutane-aδ-diol* as a colourless, viscid liquid boiling at 123° under 10 mm. pressure. Ethyl aa-dimethyl-

glutarate yields *β-dimethylpentane-αε-diol*, boiling at 134° under 10 mm. pressure. Ethyl adipate gives a small quantity of *hexane-αζ-diol*, boiling at 151° under 12 mm. pressure and melting at 35°. Ethyl β-methyladipate furnishes *γ-methylhexane-αζ-diol* as a viscid liquid boiling at 155° under 12 mm. pressure.

The methyl esters of suberic and sebacic acids are reduced easily; the former gives *octane-αθ-diol*, which distils at 172° under 20 mm. pressure, and when crystallised from a mixture of benzene and alcohol melts at 63°; the latter yields *decane-ακ-diol*, which boils at 179° under 11 mm. pressure, and crystallises from benzene in colourless crystals melting at 71·5°. J. McC.

Composition of Oleum Stillingiae. J. Klimont (*Monatsh.*, 1903, **24**, 408—412).—The fat obtained on pressing the warm seeds of *Stillingia sebifera* consists of a dipalmito-olein (glyceryl dipalmito-oleate), $C_3H_5(C_{16}H_{31}O_2)_2 \cdot C_{18}H_{33}O_2$, which melts at 29·2° and gives saponification and iodine numbers agreeing with those calculated from the formula, and a small amount of a less fusible glyceride (tripalmitin ?). G. Y.

Addition of Hydrogen Fluoride to Oxalates and Ammonium Tartrate. Rudolf F. Weinland and W. Stille (*Annalen*, 1903, **328**, 149—153).—On mixing solutions of potassium oxalate and fluoride with a warm 40 per cent. solution of hydrogen fluoride and slowly evaporating over phosphoric oxide, the *double* salt, C_2O_4HK,HF, separates in large, rhombohedric crystals, which are unstable even in dry air; in moist air, hydrogen fluoride is replaced by water. The *double* salt with rubidium hydrogen oxalate, C_2O_4HRb,HF, is similar to the potassium salt, as is also the *ammonium* salt.

When ammonium tartrate and ammonium carbonate are dissolved in 40 per cent. hydrofluoric acid and the solution concentrated over phosphoric oxide, a *double* salt, $C_4O_6H(NH_4),HF$, separates in lustrous, thick plates.

These additive compounds are sparingly soluble in water.

K. J. P. O.

Bismuth Basic Oxalates. Francis B. Allan (*J. Amer. Chem. Soc.*, 1903, **25**, 722—727. Compare Abstr., 1901, ii, 318; 1902, ii, 401).—Normal bismuth oxalate, containing some basic oxalate, was stirred with water or oxalic acid solution, and the composition of the undissolved solid was determined by analysis of the liquid phase. At 50°, the basic salt is in equilibrium with oxalic acid solution up to 0·085*N*, and at 75° up to at least 0·135*N*. The salt has the composition $Bi_2O_3,2C_2O_3,H_2O$, and, in contact with dilute ammonia and ammonium oxalate solution, is converted into another basic salt having the composition $3Bi_2O_3,2C_2O_3$. A. McK.

A New Double Oxalate of Bismuth and Potassium. Francis B. Allan and J. S. DeLury (*J. Amer. Chem. Soc.*, 1903, **25**, 728—729).—When a small quantity of bismuth oxalate is agitated with a saturated aqueous solution of potassium oxalate, the solid phase con-

sists almost entirely of potassium oxalate. When bismuth oxalate is boiled with a 20 per cent. solution of potassium oxalate, small, white crystals of the double oxalate, $Bi_2(C_2O_4)_3,K_2C_2O_4,9\frac{1}{2}H_2O$, are deposited on cooling. A. McK.

A New Double Oxalate of Bismuth and Ammonium. Francis B. Allan and J. A. Phillips (*J. Amer. Chem. Soc.*, 1903, 25, 729—730).—When a 4 per cent. solution of ammonium oxalate is boiled with bismuth oxalate for half an hour and the solution filtered, small, white crystals of the double salt, $Bi_2(C_2O_4)_3,(NH_4)_2C_2O_4,8H_2O$, are deposited on cooling. A. McK.

Esterification of Mineral Acids. Antoine Villiers (*Ann. Chim. Phys.*, 1903, [vii], 29, 561—574. Compare this vol., i, 598, 599).—The results of experiments with other alcohols confirm the conclusions arrived at from the esterification of hydrochloric acid by ethyl alcohol. The velocity of esterification decreases with increase of molecular weight for monohydric alcohols. Glycol and glycerol rapidly attain equilibrium with hydrochloric acid, even at the ordinary temperature. C. H. D.

Esters of Sulphuric Acid and of Chlorosulphonic Acid. Frank W. Bushong (*Amer. Chem. J.*, 1903, 30, 212—224).—Ethyl chlorosulphonate, prepared by the action of phosphorus pentachloride on ethyl sulphuric acid (Nef, Abstr., 1901, i, 626), is identical with the product obtained from ethyl alcohol and sulphuryl chloride (Behrend, Abstr., 1877, ii, 287). It is vigorously acted on by sodium alkyloxides in ethereal solution, and an intermediate additive product is probably formed; the products of the action are alkyl ethyl sulphate, alkyl sodium sulphate, a mixed ether, sodium sulphate, and alcohol. Since ethyl chlorosulphonate is a vigorous alkylating agent, it probably readily dissociates according to the scheme $Cl{\cdot}SO_2OEt \rightleftharpoons {>}CHMe + ClSO_2OH$ (Nef, *loc. cit.*). Experiments on the action of ethyl chlorosulphonate on sodium ethoxide, *iso*amyloxide, *iso*butoxide, and *iso*propoxide, respectively, are described.

When sulphuryl chloride is employed in place of ethyl chlorosulphonate, analogous results are obtained. A sulphite is, however, obtained as a by-product, and it is assumed that its formation is due to the action of the dissociation products of sulphuryl chloride, namely, sulphur dioxide and chlorine, on the alkyloxides.

Ethylaniline is produced by the interaction of aniline and ethyl chlorosulphonate. A. McK.

Action of Acetyl Chloride on Selenic Acid. Arthur B. Lamb (*Amer. Chem. J.*, 1903, 30, 209—212).—Selenium trioxide was not obtained by the action of phosphoric oxide, anhydrous perchloric acid, or acetyl chloride on selenic acid. When acetyl chloride is added to selenic acid at 0°, the action is very energetic, and a granular precipitate of the hygroscopic selenium tetrachloride separates; selenic acid is completely reduced under these conditions. A. McK.

Investigations on Phosphorous Acid and some of its Derivatives. A. SACHS and N. LEVITSKY. **Esterification of Phosphorous Acid.** A. SACHS. **Diethyl Phosphite.** N. LEVITSKY (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 211—218).—Experiments on the esterification of phosphorous acid by methyl, ethyl, and butyl alcohols show that the amount of ester formed soon reaches a maximum varying with the concentration and with the particular alcohol employed and that, after this has taken place, the quantity of free acid present begins to increase again. Assuming that esterification yields the di-ester (see Thorpe and Norton, Trans., 1890, 634), the author explains the above anomalous behaviour as due to the formation of an ether according to one or other of the two equations: $P(OEt)_2OH = Et_2O + PO(OH)$; $P(OEt)_2OH + 2EtOH = 2Et_2O + P(OH)_3$.

The author has prepared diethyl phosphite by the action of phosphorus trichloride on ethyl alcohol, and attributes the structure $OH \cdot P(OEt)_2$ to this compound because of (1) its preparation from a derivative in which phosphorus is trivalent, (2) its OH residue as evidenced by the energetic action of bromine according to the equation: $OH \cdot P(OEt)_2 + Br_2 = 2EtBr + PO_2 \cdot OH$, (3) the equivalence of the two ethoxy-groups, and (4) the ease with which the ester undergoes oxidation. T. H. P.

Transformation of Aldehydes and Ketones into Alcohols by Catalytic Hydrogenation. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1903, **137**, 301—303. Compare this vol., i, 393, 453, 454).—The authors find that nickel reduced at as low a temperature as possible is most efficacious for the catalytic reduction of aldehydes and ketones since the process can be carried out at a lower temperature than when another catalyst is employed. Acetaldehyde vapour mixed with hydrogen, when passed over reduced nickel at 140°, gives an almost quantitative yield of ethyl alcohol. With formaldehyde, the optimum temperature is 90°. Propaldehyde is regularly transformed into propyl alcohol at 102—145°. *iso*Butaldehyde gives *iso*butyl alcohol at 135—160°, and valeraldehyde gives amyl alcohol (b. p. 131·5°) at 135—165°. Acetone gives *iso*propyl alcohol at 115—125°, methyl ethyl ketone gives β-butanol at 130°, diethyl ketone gives γ-pentanol at 130—140°, methyl propyl ketone and ethyl *iso*propyl ketone at 130—150° give β-pentanol and β-methyl-γ-pentanol respectively, and methyl butyl ketone gives β-hexanol at 150°.

Reduced cobalt acts less energetically than reduced nickel, and the yield is smaller. Reduced copper only acts at a higher temperature and consequently much of the alcohol formed is decomposed. Platinum sponge acts too slowly, and the reduction is so incomplete that the hydrogenation cannot be carried out practically. J. McC.

The Mutual Transformation of the two Stereoisomeric Methyl-*d*-glucosides. C. L. JUNGIUS (*Proc. K. Acad. Wetensch. Amsterdam*, 1903, **6**, 99—104).—Starting with either α- or β-methylglucoside dissolved in methyl alcohol containing hydrogen chloride, the equilibrium ultimately obtained is the same in each case. After removing the hydrogen chloride by lead carbonate and evaporating

the liquid, a crystalline mass was obtained from which ethyl acetate extracted a very small quantity of a non-crystallisable product which may be the dimethylacetal of the glucoside. By determining the change in the rotatory power, it was found that, in the condition of equilibrium, the solution contains 77 per cent. of the glucoside in the α-form, and 23 per cent. in the β-form. From determinations of the velocity of reaction, it has been calculated that the reaction is a unimolecular one, and the velocity constant (time expressed in hours) is 0·0051 at 25° when the solution is $1{\cdot}34N$ with respect to hydrogen chloride. The concentration of hydrogen chloride necessary to cause the mutual transformation of the isomerides is much larger than is usually required in catalytic reactions, and therefore the possibility that the hydrogen chloride actually takes part in the reaction is not excluded. Further, the constants obtained for different hydrogen chloride concentrations point to a more rapid increase in the velocity with rising hydrogen chloride concentration than that required by simple proportionality. Fischer (Abstr., 1895, i, 437) has suggested that the transformation is due to the intermediary formation of the dimethylacetal, α-glucoside $\rightleftarrows$ acetal $\rightleftarrows$ β-glucoside. This would only agree with the author's results if the decomposition of the acetal takes place with an extraordinary rapidity. In order to test this, the dimethylacetal was prepared and dissolved in a $2N$ solution of hydrogen chloride in methyl alcohol, and it was found that the decomposition is by no means rapid. Besides this, the transformation of the α-form into the β-variety takes place in ethyl alcohol in just the same way as in methyl alcohol, and therefore the balance of evidence is in favour of the mutual transformation being direct: α-glucoside $\rightleftarrows$ β-glucoside.

For a hydrogen chloride concentration of $1{\cdot}07N$ in methyl alcohol, the velocity constant is 0·0040. If 1 mol. of water per mol. of hydrogen chloride is added, the constant is reduced to 0·0012, and if the amount of water be increased to 5 mols. per mol. of hydrogen chloride, the constant is diminished to 0·0001.

The presence of hydrogen chloride seems to be essential for the transformation; the β-glucoside was kept fused for some time, but on cooling it was found that no change had taken place. Zinc chloride is incapable of causing the transformation in methyl alcohol solution.

The rotatory power of a solution of methylmannoside in methyl alcohol containing hydrogen chloride slowly decreases without formation of mannose; this change may be due to the formation of a β-isomeride which has not yet been isolated. J. McC.

Carbohydrates from Serum Globulins. Leo Langstein (*Monatsh.*, 1903, 24, 445—476. Compare Abstr., 1903, i, 374). —When acted on by phenylhydrazine, the mixture of carbohydrates, obtained, to the extent of 1·4 per cent., on boiling the globulin from the blood-serum of horses with 5 per cent. hydrobromic acid, yields glucosazone melting at 204—205°, an osazone which forms dark brown, spherical aggregates and melts at 171—196°, and a quantity of oily products. Oxidation of the carbohydrates with nitric acid leads to the formation of saccharic acid.

When acted on by benzoyl chloride and sodium hydroxide, the

carbohydrates yield a mixture of benzoyl derivatives. The derivative melting at 162—168° has the composition of tetrabenzoyldextrose, containing a small amount of the pentabenzoyl derivative, and yields dextrose on hydrolysis with sodium ethoxide. The product, which crystallises in snow-white needles and melts at 196°, is a benzoylaminohexose, but not a glucosamine derivative. The remainder of the benzoylated product yields, on hydrolysis, lævulose and a lævorotatory, non-fermentable carbohydrate, which forms an osazone crystallising in spherical aggregates and melting at 184—186°.

As the mixture of carbohydrates gives only a very faint Seliwanoff's reaction, the lævulose obtained by hydrolysing the benzoyl derivative may have been formed from the dextrose by isomeric change (compare Bruyn and Ekenstein, Abstr., 1896, i, 116). G. Y.

The Sugar of Buffalo's Milk. CH. PORCHER (*Bull. Soc. chim.*, 1903, [iii], 29, 828—830. Compare Strohmer, Abstr., 1888, 976, and Pappel and Richmond, Trans., 1890, **57**, 754).—The author finds that the milk of the Egyptian buffalo contains lactose but no new sugar (tewfikose), as was asserted by Pappel and Richmond (*loc. cit.*). The sugar was isolated by precipitating the casein with acetic acid, neutralising the filtrate with sodium hydroxide solution, and extracting the residue left on evaporation with acetone. Lactose was also isolated from other samples of milk obtained from buffaloes in Italy and Annam. T. A. H.

Condensations by Zinc Chloride. MARCEL DESCUDÉ (*Ann. Chim. Phys.*, 1903, [vii], 29, 486—560. Compare Abstr., 1901, i, 357, 504, 644; 1902, i, 149, 339, 451, 738, and this vol., i, 600).—A detailed account is given of a large number of condensations described in the earlier papers, and the mechanism of the reactions is discussed. In studying the action of amines on methylene dibenzoate, a number of benzoates of amines were prepared. *Methylamine hydrogen benzoate*, $C_6H_5\cdot CO_2\cdot NH_3Me,C_6H_5\cdot CO_2H$, melts at 110° and dissolves in water or alcohol, but not in ether, benzene, or chloroform. *Dimethylamine hydrogen benzoate*, $C_6H_5\cdot CO_2\cdot NH_2Me_2,C_6H_5\cdot CO_2H$, melts at 127° and dissolves readily in alcohol, but very sparingly in water, ether, or benzene. The *benzoates* of *trimethylamine*, *ethylamine*, and *diethylamine* are also acid salts melting at 113°, 92°, and 100—101°. *Dipropylamine benzoate* is a normal salt, $C_6H_5\cdot CO_2\cdot NH_2Pr^a{}_2$, melting at 107—108°. The normal *benzoates* of iso*butylamine*, diiso*butylamine*, and *benzylamine* melt at 135—136°, 92—93°, and 128° respectively. *Dibenzylamine* forms a *normal benzoate* melting at 94°, and an *acid* salt melting at 111°. Only the benzoates of the secondary amines are sufficiently soluble in benzene or ethylene dibromide to allow of cryoscopic measurements, which indicate considerable association of the dissolved molecules. C. H. D.

Action of Nitrous Acid on $\alpha\theta$-Octomethylenediamine. EMMO LOEBL (*Monatsh.*, 1903, 24, 391—407. Compare Solonina, Abstr., 1899, i, 562).—The successive action of silver nitrite and dilute sulphuric acid on $\alpha\theta$-octomethylenediamine hydrochloride leads to the

formation of an unsaturated alcohol, a diprimary glycol, a primary-secondary glycol, and a trace of an unsaturated hydrocarbon, C_8H_{14} (?).

The *unsaturated alcohol*, $C_8H_{16}O$, boils at 188—193° under 760 mm. pressure. A fraction, boiling at 183—187°, contains probably the same alcohol. It is an oil, has an odour resembling octyl alcohol, is almost insoluble in water, easily soluble in alcohol or ether, and yields an *acetate*, which boils at 207·9° (corr.) under 757·3 mm. pressure. When oxidised with potassium permanganate, it yields acetic and adipic acids, and must be represented by the constitutional formula, $CHMe{:}CH{\cdot}[CH_2]_4{\cdot}CH_2{\cdot}OH$.

The *diprimary glycol*, $C_8H_{18}O_2$, crystallises in white needles, melts at 58·5°, boils at 162—165° under 11 mm. pressure, is easily soluble in alcohol or chloroform, less so in water, ether, or benzene, yields a *diacetate*, $C_{12}H_{22}O_4$, boiling at 163—168° under 11 mm. pressure, and, on oxidation with potassium permanganate, gives rise to suberic acid.

The *primary-secondary glycol*, $C_8H_{18}O_2$, is obtained in two fractions boiling at 151—157° under 15 mm. and at 156—159° under 11 mm. pressure. G. Y.

Condensation of Ethyl Oxalate with Ethylene and Trimethylene Dicyanides. ARTHUR MICHAEL (*Amer. Chem. J.*, 1903, **30**, 156—162).—Ethyl oxalate condenses with succinonitrile in the presence of sodium or alcoholic sodium ethoxide to *ethyl βγ-dicyano-αδ-diketoadipate*, $\begin{array}{l}CN{\cdot}CH{\cdot}CO{\cdot}CO_2Et\\ CN{\cdot}\overset{|}{C}H{\cdot}CO{\cdot}CO_2Et\end{array}$, a compound crystallising from alcohol in long, straw-coloured prisms, which often form fan-shaped groups; it separates from benzene in small, prismatic needles, which melt at 121—123°. The *sodium* derivative melts at 92—96°. Ethyl oxalate also condenses readily with trimethylene dicyanide to form *ethyl βδ-dicyano-α-ketoglutarate*, $\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CN\\ CN{\cdot}\overset{|}{C}H{\cdot}CO{\cdot}CO_2Et\end{array}$, which crystallises from benzene in almost white, six-sided prisms, and melts at 96—98°; it is readily soluble in hot water or benzene, but only sparingly so in ether, light petroleum, or carbon tetrachloride. No formation of ring compounds could be observed. C. H. D.

Condensation of Aldehydes with Ethyl Cyanoacetate. II. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1902—1903, **38**, 290—300. Compare Abstr., 1902, i, 819).—*iso*Butaldehyde, ethyl cyanoacetate, and ammonia yield the ammonium salt of the corresponding glutaconimide (Abstr., 1900, i, 111) and *iso*butylcyanoacetamide, $CHMe_2{\cdot}CH_2{\cdot}CH(CN){\cdot}CO{\cdot}NH_2$, which separates from water in broad laminæ melting at 104—104·5° and boiling at 275—280° under 745 mm. pressure; it is soluble in alcohol, ether, or chloroform. Henry (*Bull. Acad. roy. Belg.*, 1889, **18**, 684) describes this compound as being insoluble in ether or chloroform and melting at 93°. This author (*loc. cit.*) also gave the melting point of α-cyanopropionamide as 81°, whilst in the author's laboratory Beccari found 100°.

Propaldehyde, ethyl cyanoacetate, and ammonia yield also the ammonium salt of the corresponding substituted glutaconimide and

propylcyanoacetamide; the latter separates from ether in thin, shining laminæ soluble in water, alcohol, or chloroform, and melts at 124—124·5°; Henry (*loc. cit.*) gave 118° as the melting point of this compound, which he described as insoluble in ether or chloroform.

*iso*Valeraldehyde, ethyl cyanoacetate, and ammonia yield: (1) a small quantity of iso*amylcyanoacetamide*, $CHMe_2\cdot[CH_2]_2\cdot CH(CN)\cdot CO\cdot NH_2$, which crystallises from aqueous alcohol in long, shining needles, melts at 142·5°, and boils without decomposition; it is soluble in pyridine and to a slight extent in water, giving a neutral solution, and does not absorb bromine; (2) the *ammonium* derivative of iso*butyldicyanoglutaconimide* (3 : 5-*dicyano*-2 : 6-*dioxy*-4-iso*butylpyridine*),

$$CHMe_2\cdot CH_2\cdot C{<}{CH(CN)\cdot CO \atop C(CN)-CO}{>}N\cdot NH_4,$$

which crystallises from water in long, silky, anhydrous needles and is soluble in alcohol; the corresponding *potassium*, *coniine*, *nickel*, *silver* $(+H_2O)$, basic or normal *copper*, $C_{11}H_9O_2N_3Cu$, and *cobalt* (+7 or $5H_2O$) derivatives were prepared.

Heptaldehyde, ethyl cyanoacetate, and ammonia yield: (1) the *ammonium* derivative of *hexyldicyanoglutaconimide* (3 : 5-*dicyano*-2 : 6-*dioxy*-4-*hexylpyridine*), $CH_3\cdot[CH_2]_5\cdot C{<}{CH(CN)\cdot CO \atop C(CN)-CO}{>}N\cdot NH_4$, which crystallises from water in shining, slender needles soluble in alcohol or pyridine; the corresponding *cuprammonium*, *nicotine*, *coniine*, *quinine*, and *cinchonine* derivatives were prepared; (2) *heptylcyanoacetamide*, $CH_3\cdot(CH_2)_6\cdot CH(CN)\cdot CONH_2$, which crystallises from alcohol in slender, nacreous laminæ, melts at 137·5°, and is very soluble in pyridine. T. H. P.

Double and Triple Thiocyanates of Cæsium, Cadmium, and Silver. HORACE L. WELLS (*Amer. Chem. J.*, 1903, 30, 144—154).—The following new salts are described: $CsCd(SCN)_3$, tablets or prisms, melting at 212—214°; $Cs_4Cd(SCN)_6,2H_2O$, tablets, melting when anhydrous at 110—120°; $CdAg_2(SCN)_4,2H_2O$; $Cs_2CdAg_2(SCN)_6,2H_2O$, prisms, losing water on exposure; $Cs_2CdAg_2(SCN)_6$, brilliant scales; $Cs_2CdAg_4(SCN)_8,2H_2O$, minute, hexagonal prisms;

$$Cs_4Cd_3Ag_{10}(SCN)_{20},6H_2O,$$

large, rhombic crystals. In spite of its complicated formula, the last of these triple salts appears to be a definite substance (compare also this vol., i, 154). C. H. D.

Rubidium Barium Silver Thiocyanates. HORACE L. WELLS (*Amer. Chem. J.*, 1903, 30, 184—187. Compare this vol., i, 154).—*Rubidium barium silver thiocyanate*, $Rb_4BaAg_2(CNS)_8,H_2O$, forms prismatic crystals and corresponds in type to the potassium barium silver salt previously described. A salt of the composition $Rb_2BaAg_2(CNS)_6,2(?)H_2O$ was occasionally obtained instead. Both salts are very soluble in water and crystallise unsatisfactorily.

A. McK.

Secondary Amides. TARBOURIECH (*Compt. rend.*, 1903, 137, 326—327. Compare this vol., i, 681).—By the process already

described, the following asymmetric secondary amides have been prepared. *Butyropropionamide*, white, leafy crystals melting at 109°. iso*Butyropropionamide*, fine needles melting at 140°. iso*Valeropropionamide*, white, aggregated needles melting at 68°. iso*Butyrobutyramide*, melting at 103°. iso*Valerobutyramide*, melting at 88°. iso*Butyro*iso*valeramide*, melting at 94°. iso*Butyrovaleramide*, melting at 84°. The secondary amides are soluble in alcohol, benzene, and xylene, and very soluble in ether. By evaporating a xylene solution, they are obtained in well-crystallised forms. The solubility in water diminishes as the percentage of carbon in the compound increases. They volatilise readily at temperatures below their melting points. They do not easily combine with metallic chlorides, and thus do not form platinichlorides or aurichlorides; they do not combine with picric acid. The introduction of a second acidyl group into propionamide diminishes the basic character. Dipropionamide is very readily hydrolysed by mineral acids.
J. McC.

Hydantoin and the Isomerism of the Methylhydantoins. Carl D. Harries and Maurus Weiss (*Annalen*, 1903, **327**, 355—384. Compare Abstr., 1901, i, 71).—For the three isomeric methylhydantoins hitherto described, a systematic nomenclature is suggested, thus:

$$CO{<}{\scriptstyle \alpha\ \beta\ \epsilon}\begin{matrix} NH{\cdot}CH_2 \\ {\scriptstyle \gamma}\,|\,{\scriptstyle \delta} \\ NH{\cdot}CO \end{matrix}.$$

γ-Methylhydantoin was prepared by Urech (*Annalen*, 1873, **165**, 199); β-methylhydantoin, prepared by Neubauer (*Annalen*, 1866, **137**, 288) from creatinine, melts at 156°, and ϵ-methylhydantoin, prepared by Franchimont and Klobbie (Abstr., 1889, 1143), melts at 184°.

The preparation of ethyl hydantoate and hydantoin from the ethyl ester of glycine is here described in detail (compare *loc. cit.*).

Ethyl thiohydantoate, $NH_2{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, prepared in a similar manner from the hydrochloride of the ethyl ester of glycine and potassium thiocyanate, forms crystals melting at 65°, but cannot be converted into thiohydantoin. Attempts to prepare this compound by the action of ammonium sulphide on hydantoin also failed.

On attempting to reduce β-nitrohydantoin (Franchimont and Klobbie, m. p. 170°) with stannous chloride, no aminohydantoin, but only hydantoin, was obtained.

β-Acetylhydantoin, $CO{<}\begin{matrix} NAc{\cdot}CH_2 \\ NH{-}CO \end{matrix}$, was prepared by heating hydantoin for several hours with acetic anhydride; it crystallises in needles melting at 143—144° and forms an insoluble, crystalline lead salt.

Whereas the potassium salt of hydantoin and methyl iodide yield ϵ-methylhydantoin, it is found that a new methylhydantoin, *iso*-ϵ-methylhydantoin, for which a hydroxy-formula, $OH{\cdot}C{\lessdot}\begin{matrix} N{-\!\!-}CH_2 \\ NMe{\cdot}CO \end{matrix}$, is suggested, is obtained by heating silver hydantoate with methyl iodide under pressure at 110—120°; it is separated from the unchanged hydantoin by sublimation, and crystallises in needles melting at 171°;

on evaporating with concentrated nitric acid, it is converted into a nitro-derivative melting at 168°, and identical with that prepared by Franchimont and Klobbie (*loc. cit.*) from ε-methylhydantoin.

ε-Ethylhydantoin, prepared from the potassium salt of hydantoin and ethyl iodide, crystallises in transparent prisms melting at 102°; the silver salt of hydantoin does not react with ethyl iodide to give an ethylhydantoin. *β-Nitro-ε-ethylhydantoin*, prepared in a similar manner to the corresponding methyl derivative, crystallises in leaflets melting at 95—96°.

Dichlorohydantoin, $CO<\begin{matrix}NH\cdot CCl_2\\ NH\cdot CO\end{matrix}$(?), was finally obtained by passing chlorine through an aqueous solution of hydantoin exposed to sunlight, when lustrous needles separated melting at 120—121°; in solution in all solvents, it is very unstable, and is converted both by ammonia and by silver oxide into hydantoin.

Ethyl lacturamate, $NH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2Et$, is prepared by digesting a concentrated aqueous solution of the hydrochloride of the ethyl ester of alanine with potassium cyanate, and is a hygroscopic substance crystallising in needles melting at 93—94°. On boiling with hydrochloric acid, alcohol is eliminated and lactylcarbamide (m. p. 145°) is formed. The *acetyl* derivative, prepared by boiling with acetic anhydride, crystallises in six-sided leaflets melting at 129—131°. K. J. P. O.

Oxidation of Trimethyluracil. Robert Behrend and Ludwig Fricke (*Annalen*, 1903, **327**, 253—268).—The behaviour of trimethyluracil towards permanganate has been investigated, as a continuation of the study of the oxidation of methyl- and dimethyl-uracils (Abstr., 1900, i, 120; and *ibid.*, 1902, i, 832). When the oxidation is carried out in the cold (at 10—15°), dimethylparabanic acid, which crystallises in rhombic leaflets melting at 149—150°, is the main product. Neither acetyldimethylcarbamide nor dimethyloxaluric acid was found. Dimethylparabanic acid is, however, not resolved by alkalis into the acid last mentioned, but with baryta water or ammonia yields dimethylcarbamide, and with a small quantity of potassium hydroxide or potassium hydrogen carbonate, dimethyloxamide (which crystallises in needles or leaflets melting at 209—210°). This amide is always found in small quantities as a product of the oxidation of trimethyluracil, and is the exclusive product when the oxidation is carried out at a high temperature. This fact renders it probable that parabanic and methylparabanic acids are respectively formed as intermediate products in the oxidation of methyl- and dimethyl-uracils (*loc. cit.*).

In addition to the substances just mentioned, methyloxaluric acid and *hydroxy-β-dimethyluracil*, $\begin{matrix}CO\cdot C(OH)\vdots CMe\\ \vert \qquad\qquad \vert\\ NMe-CO-NH\end{matrix}$, are formed in the oxidation of trimethyluracil in the cold; the latter substance, which is obtained in quantity by treatment of trimethyluracil with acid permanganate (1 atom of oxygen), crystallises in rhombic leaflets, and with ferric chloride gives an intense blue coloration. On further oxidation, it yields acetylmethylcarbamide and methyloxaluric acid.

Since it is produced in such unexpectedly large quantities, it is possible that it is partly formed from some impurity present in the trimethyluracil, which itself might be expected to yield mainly hydroxytrimethyluracil.

Although *trihydroxydihydromethyluracil* (II) could not be isolated as an intermediate product in the oxidation of methyluracil (*loc. cit.*), this substance may be obtained at least in solution by treating dibromohydroxytrimethyluracil (I) with excess of potassium hydroxide; on evaporating and extracting with ether, a change takes place, and the *C-acetyldimethylallanturic acid* (III) is isolated as a colourless, hygroscopic syrup, which gives an intense blue coloration with ferric chloride, thus:

$$\text{(I)}\ \begin{matrix} CO\cdot CBr_2\cdot CMe\cdot OH \\ NMe\cdot CO\cdot NMe \end{matrix} \longrightarrow \text{(II)}\ \begin{matrix} CO\cdot C(OH)_2\cdot CMe\cdot OH \\ NMe\cdot CO\text{——}NMe \end{matrix}$$

$$\longrightarrow \text{(III)}\ \begin{matrix} CO\text{———}CAc\cdot OH \\ NMe\cdot CO\cdot NMe \end{matrix}.$$

The view that a five-membered ring is present in this acid instead of the pyrimidine-ring finds support in the ready conversion of this compound into dimethylparabanic acid by oxidation with chromic acid. Moreover, on reduction with zinc dust in acid solution, hydroxytrimethyluracil is not regenerated. K. J. P. O.

Preparation of Thioxanthine. C. F. BOEHRINGER & SOEHNE (D.R.-P. 141974 and 142468. Compare Abstr., 1902, i, 505; also Fischer and Tüllner, Abstr., 1902, i, 664).—An alkaline solution of *iso*uric acid absorbs hydrogen sulphide, forming a salt of γ-thio-ψ-uric acid, which is converted by boiling with mineral acids into thioxanthine (2 : 6-dihydroxy-8-thiopurine).

Thioxanthine may also be prepared by warming 4 : 5-diamino-2 : 6-dihydroxypyrimidine (4 : 5-diaminouracil) with carbon disulphide and potassium hydroxide:

$$\begin{matrix} NH\cdot CO-C\cdot NH_2 \\ CO\cdot NH\cdot C\cdot NH_2 \end{matrix} + CS_2 = \begin{matrix} NH\cdot CO-C\cdot NH \\ CO\cdot NH\cdot C\cdot NH \end{matrix}\!\!>\!CS + H_2S.$$

C. H. D.

Crotonaldazine and its Conversion into 5-Methylpyrazoline. JAROSLAV HLADÍK (*Monatsh.*, 1903, 24, 434—444. Compare von Rothenburg, Abstr., 1895, i, 688).—*Crotonaldazine*, obtained by the action of crotonaldehyde on hydrazine in aqueous solution and purified by sublimation under 12 mm. pressure, forms sulphur-yellow needles and prismatic crystals, melts at 96°, has a characteristic aromatic odour, is easily soluble in alcohol, acetone, or benzene, but less so in ether, and yields crotonaldehyde when boiled with dilute sulphuric acid. The *hydrochloride*, $C_8H_{12}N_2,HCl$, formed by the action of hydrogen chloride on the aldazine in ethereal solution, is a reddish-yellow, viscous mass. The residue from the sublimation contains a *polymeride* of crotonaldazine, $(C_8H_{12}N_2)_2$, which forms a brownish-yellow, amorphous powder, changes to a brown, viscous mass at 95—100°, is easily soluble in alcohol, acetone, or benzene, and yields crotonaldehyde when boiled with dilute sulphuric acid.

When heated with hydrazine hydrate in a sealed tube at 120°,

crotonaldazine is converted into 5-methylpyrazoline, which boils at 52° under 12 mm. pressure (Curtius and Zinkeisen, Abstr., 1899, i, 166).

G. Y.

A New Class of Organo-Tin Compounds containing Halogens. William J. Pope and Stanley J. Peachey (*Proc. Roy. Soc.*, 1903, 72, 7—11).—Most of the organo-tin compounds hitherto described have been derivatives of the hypothetical stannimethane, SnH_4, and this series is now completed by the preparation of compounds corresponding in constitution with chloroform. *Methylstanniodoform*, $CH_3{\cdot}SnI_3$, prepared by warming tetramethylstannimethane with stannic iodide, crystallises from ether or light petroleum in long, straw-yellow needles or prisms melting at 82—84°, and volatilising when heated gently. It is odourless, and dissolves readily in alcohol, acetone, or benzene. Warming with sodium hydroxide converts it into *methylstannoxylic acid*, $CH_3{\cdot}SnO_2H$, which is identical with the compound obtained by G. Meyer by the action of methyl iodide on sodium stannite (Abstr., 1883, 1078). The acidic properties of the acid are very weak, and no salts could be prepared. Boiling with concentrated alkali hydroxides causes evolution of methane, with formation of trimethylstannicarbinol, $SnMe_3{\cdot}OH$, and dimethylstannimethylene oxide, $SnMe_2O$. Hydriodic acid converts it again into methylstanniodoform. In the same way, hydrobromic acid forms *methylstannibromoform*, $CH_3{\cdot}SnBr_3$, crystallising from petroleum in colourless prisms, melting at 50—55°, and dissolving in water; and hydrochloric acid forms *methylstannichloroform*, $CH_3{\cdot}SnCl_3$, crystallising from light petroleum in colourless prisms, which melt at 105—107° and distil undecomposed at 179—180°; it fumes in air and dissolves in water and organic solvents.

C. H. D.

***cyclo*Trimethylene Compounds.** Arthur Kötz and G. Stalmann (*J. pr. Chem.*, 1903, [ii], 68, 156—173).—*Ethyl 1-methyl*cyclo*trimethylene-2 : 2 : 3 : 3-tetracarboxylate*, formed by the action of bromine on ethyl disodioethylidenedimalonate, is a viscid, colourless oil which crystallises slowly. When distilled in a vacuum at 185—195°, it decomposes with formation of ethyl ethylenetetracarboxylate. 1-*Methyl*cyclo*trimethylene-2 : 3-dicarboxylic acid*, obtained from the tetraethyl ester, is a syrup; it yields a *silver* salt, $C_6H_6O_4Ag_2,\frac{1}{2}H_2O$, and an insoluble *barium* salt, and forms an *ethyl ester* which boils at 198—200° under 14 mm. pressure. The stability of the acid towards bromine is similar to that of trimethylenedicarboxylic acid; when distilled in a vacuum, it yields ethylmaleic acid.

The action of sodium on ethyl benzylidenemalonate and ethyl malonate in ethereal solution, leads to the formation of *ethyl benzylidenedimalonate*, which distils at 225—230° under 14 mm. pressure.

*Ethyl 1-phenyl*cyclo*trimethylene-2 : 2 : 3 : 3-tetracarboxylate*, formed by the action of bromine on ethyl disodiobenzylidenedimalonate, is a viscid oil which decomposes at 100—200° under 12 mm. pressure, yielding benzaldehyde and ethyl ethylenetetracarboxylate. Hydrolysis of the tetraethyl ester leads to the formation of *cis*-phenyl*cyclo*trimethylene-2 : 3-dicarboxylic acid.

The action of ethyl ethylidenetetracarboxylate on ethyl disodiomalonate leads to the formation of *ethyl propanehexacarboxylate*, which, on hydrolysis, yields tricarballylic and propanetetracarboxylic acids. *Ethyl* cyclo*trimethylenehexacarboxylate*, formed by the action of bromine on ethyl disodiopropanehexacarboxylate, is a viscid, yellow oil, which distils unchanged at 197—202° under 12 mm. pressure, and, on hydrolysis, yields trimethylene-1 : 2 : 3-tricarboxylic acid.

Ethyl *cyclo*trimethylenetetracarboxylate is obtained in two modifications by the action of methylene di-iodide on ethyl disodioethanetetracarboxylate. One of these is an oil which boils at 158—160° under 14 mm. pressure, and, on hydrolysis, yields *trans-cyclo*trimethylene-2 : 3-dicarboxylic acid ; the other form (Guthzeit and Dressel, Abstr., 1890, 879) crystallises in slender needles, melts at 43°, and, on hydrolysis, yields *cis-cyclo*trimethylene-2 : 3-dicarboxylic acid.

The action of ethylidene di-iodide or of $\beta\beta$-dichloropropane on ethyl disodioethanetetracarboxylate leads to the formation of ethyl succinate, but not of trimethylene derivatives. G. Y.

Fission Phenomena in the Trimethylene (*cyclo*Propane) Group. ARTHUR KÖTZ (*J. pr. Chem.*, 1903, [ii], 68, 174—189).—The work of various authors on the stability of the trimethylene ring is reviewed and the following general rules deduced :

The stability of the trimethylene ring is diminished by the presence of an alkyl or acyl radicle and increased by a carboxyl group.

1 : 1-Dimethyltrimethylene is less stable than methyltrimethylene.

With the exception of trimethylene-1 : 1-dicarboxylic acid, the polycarboxylic acids of the group are characterised by their great stability.

Simultaneous substitution by a carboxyl group and an alkyl or a phenyl radicle decreases the stability. In the presence of an alkyl or a phenyl group, the instability has been observed to increase with the number of carboxyl groups. G. Y.

Formation of *cyclo*Pentane Compounds. ARTHUR KÖTZ and PAUL SPIESS (*J. pr. Chem.*, 1903, [ii], 68, 153—155. Compare Abstr., 1902, i, 12; this vol., i, 700).—Ethyl *cyclo*pentane-1 : 1 : 2 : 2-tetracarboxylate is formed by the action of trimethylene dibromide on ethyl disodioethanetetracarboxylate.

Ethyl *cyclo*trimethylene-1 : 1 : 3 : 3-tetracarboxylate could not be obtained by action of ethylene dibromide on ethyl disodiopropanetetracarboxylate. G. Y.

Remarks on Rupe's Communication "Influence of the Double Linking between Carbon Atoms on the Rotatory Power." JULIUS W. BRÜHL (*Annalen*, 1903, 328, 256—259).—The author comments on Rupe's statement (this vol., i, 565) that little stress can be laid upon the mol. refractions of benzene and the hydrobenzenes as evidence of the similar constitution of these compounds. It is pointed out that the density, refractive index, and the mol. volume, as well as the mol. refraction, vary evenly from benzene to hexahydrobenzene without any marked discontinuity at any stage, but that an exceptionally large alteration does occur in all the constants at the change from hexahydrobenzene

to hexane. Rupe's conclusion that the relationship existing in the case of the mol. refraction is only apparent and due to experimental errors is therefore quite unjustifiable. K. J. P. O.

New *p*-Menthadiene from Dihydrocarvylamine. CARL D. HARRIES (*Annalen*, 1903, 328, 322—326. Compare this vol., i, 613).—Carvoxime can be very simply prepared from carvone (as can the oximes of $\Delta^{\alpha\beta}$-ketones) by keeping a mixture of the ketone and hydroxylamine hydrochloride dissolved in methyl alcohol for several days. On distilling the phosphate of dihydrocarvylamine, prepared from the oxime (*loc. cit.*), a liquid mixture of hydrocarbons boiling at 63—64° under 10 mm. pressure, and at 177—179° under the ordinary pressure, is obtained. It has sp. gr. 0·8457 at 21°/21°, n_D 1·48895 at 21°, and $[\alpha]_D$ − 28° at 20°. The terpinene, which was present in the mixture, was separated from the terpene by treating a solution of the oil in acetic acid with sodium nitrite, when the terpinene nitrosite crystallises out. The pure menthadiene boils at 174—176° under 766 mm. pressure, and does not yield a solid hydrobromide or tetrabromide; it is practically inactive (− 3° in a 20 cm. tube at 22°), has a sp. gr. 0·8441 at 27°/27°, and n_D 1·48451 at 27°. It gives an orange-red coloration with sulphuric acid, and reddens with acetic anhydride and sulphuric acid; like all terpenes, it is rapidly destroyed by chromic acid mixture, but is otherwise very stable and can be heated to 300° without change.

In all probability the new terpene is *p-menthadiene*,

$$CMe{<}{\begin{matrix}CH{-}CH\\CH_2{\cdot}CH_2\end{matrix}}{>}CPr^{\beta},$$

and is one of the intermediate products of the transformation of dihydrocarvylamine into a terpinene, thus: dihydrocarvylamine ⟶ limonene ⟶ terpinolene ⟶ terpene ⟶ terpinene. This view is supported by the fact that on oxidation with permanganate, succinic acid is the main product; further, the abnormal mol. refraction points to the presence of an *iso*propyl group. It is highly probable that this substance occurs in natural terpenes. K. J. P. O.

Action of Alkalis and Alcohols on Chloronitrobenzene. K. BRAND (*J. pr. Chem.*, 1903, [ii], 68, 208. Compare this vol., i, 371).—The author confirms his results, which agree with those of Heumann (*Ber.*, 1872, 5, 912). Lobry de Bruyn's failure to find *o*-chloroaniline amongst the products of reduction of *o*-chloronitrobenzene with sodium ethoxide (Abstr., 1891, 429) was due to the small amount of material employed by that author. G. Y.

Derivatives of *m*-Iodotoluene containing Polyvalent Iodine. CONRAD WILLGERODT and THEODOR UMBACH (*Annalen*, 1903, 327, 269—285).—m-*Iodosotoluene*, $C_6H_4Me{\cdot}IO$, prepared from *m*-tolyl iodochloride by the action of sodium hydroxide, is a yellowish-white, amorphous powder exploding at 206—207°. The *chloride*, $C_6H_4Me{\cdot}ICl_2$, prepared by the long-continued passage of chlorine through a solution of *m*-iodotoluene in petroleum, crystallises in yellow needles decomposing at 104°, and is slowly transformed on keeping into a red liquid which

fumes in the air. With the exception of the basic sulphate, the salts are fairly stable; the *acetate*, $C_6H_4Me{\cdot}I(OAc)_2$, crystallises in colourless needles melting at 148°; the *basic nitrate*, $C_6H_4Me{\cdot}I(OH){\cdot}NO_3$, is a yellow powder melting at 79°; the *basic sulphate*,

$$[C_6H_4Me{\cdot}I(OH)]_2SO_4,$$

a white powder melting at 50°; the *basic chromate*,

$$[C_6H_4Me{\cdot}I(OH)]_2CrO_4,$$

explodes at 55°, and the *basic perchlorate*, $C_6H_4Me{\cdot}I(OH)ClO_4$, which crystallises in yellow leaflets, explodes at 125°; the basic *iodate* is a white powder.

m-*Iodoxytoluene*, $C_6H_4Me{\cdot}IO_2$, is prepared by treating an intimate mixture of *m*-tolyl iodochloride and concentrated bleaching powder solution with a little hydrochloric acid; it crystallises in lustrous leaflets exploding at 220°.

Di-m-*tolyliodinium hydroxide*, prepared by Meyer and Hartmann's method (Abstr., 1894, i, 242, 461), can only be obtained in solution; the *chloride*, $I(C_6H_4Me)_2Cl$, crystallises in white needles melting at 206°, and the *mercurichloride*, $I(C_6H_4Me)_2Cl,HgCl_2$, in white needles melting at 125°; the *platinichloride* is an orange-yellow precipitate melting at 185°; the *bromide* forms yellow leaflets melting at 146°; the *iodide*, colourless needles melting at 155°; the *nitrate*, colourless needles melting at 145°; and the *dichromate*, lustrous needles melting at 113° and exploding between 123° and 130°.

Phenyl-m-*tolyliodinium hydroxide* is prepared in the same manner as the preceding base; its *chloride* crystallises in white leaflets melting at 213°, and the *mercurichloride* in lustrous needles melting at 136°; the *platinichloride* is a yellow precipitate decomposing at 180°. The *bromide* is a white precipitate melting at 193°, and the *iodide* forms pale yellow needles melting at 165°; the *nitrate* is a white powder melting at 165—166°.

m-*Tolyl*-o-*tolyliodinium hydroxide* can be obtained as a fairly concentrated aqueous solution by treating a mixture of molecular proportions of *o*-iodosotoluene and *m*-iodoxytoluene with a suspension of silver oxide in water at 60°. The *chloride* crystallises in leaflets melting at 183—185°, and the *mercurichloride* in needles melting at 124°; the *platinichloride* is a yellow, amorphous powder melting at 188°. The *bromide* crystallises in white needles melting at 172°, and the *iodide* in needles melting at 150°, which rapidly become yellow on exposure to light; the *nitrate* forms thin plates melting at 159°.

m-*Tolyl*-p-*tolyliodinium hydroxide* is prepared like the compound last mentioned, from *p*-iodoso- and *p*-iodoxy-toluenes. The *chloride* crystallises in prisms melting at 186°; the *platinichloride* is a yellow precipitate melting at 174°. The *bromide* crystallises in white needles melting at 184°, and the *iodide* in pale yellow needles melting at 143°. The *cyanide* is a yellow powder, which becomes dark on keeping; it melts at 104—108°, and is decomposed on boiling with sodium hydroxide into *m*-iodotoluene, sodium cresoxide, and sodium cyanide. The *nitrate* forms plate-like crystals.

Iododi-m-*tolyliodinium hydroxide*, $IC_6H_3Me{\cdot}I(C_6H_4Me){\cdot}OH$, is obtained by dissolving *m*-iodosotoluene in sulphuric acid cooled to −5°, and then cautiously diluting the solution of the iodinium sulphate

with ice; the addition of a solution of potassium iodide precipitates the iodide, from which the hydroxide can be prepared by treatment with moist silver oxide. The *chloride* melts at 160°, the yellow *platinichloride* at 120°; the colourless *bromide* melts at 154°, and the yellow *iodide* at 105°; the *dichromate* is pale yellow and melts at 90—94°.

Dichloroethyl-m-*tolyliodinium hydroxide* cannot itself be obtained, but the *chloride*, $C_2H_3Cl_2 \cdot I(C_6H_4Me)Cl$, is formed when *m*-tolyl iodochloride (2 mols.) and acetylene silver chloride (1 mol.) are shaken together in aqueous suspension; it forms crystals melting at 174°. The *platinichloride* crystallises in yellow needles melting and decomposing at 135°. The *bromide* is a white, crystalline precipitate melting at 166°, and the *iodide* a yellow precipitate melting at 101°.

K. J. P. O.

Derivatives of *p*-Iodoethylbenzene containing Polyvalent Iodine. CONRAD WILLGERODT and WILLY BERGDOLT (*Annalen*, 1903, **327**, 286—300).—The *p*-aminoethylbenzene, which was used in the preparation of the compounds described in this communication, was obtained by heating aniline (3 parts), absolute alcohol (1·5 parts), and zinc chloride (4 parts) in an autoclave at 280°; the base was purified by conversion into its sulphate, which melted at 239°, and was then treated in the usual manner with nitrous acid and potassium iodide in order to prepare *p*-iodoethylbenzene; the latter is a liquid boiling at 209·01° (corr.) under 736 mm. pressure.

p-*Ethylphenyl iodochloride*, $C_6H_4Et \cdot ICl_2$, prepared by passing dry chlorine into a cooled solution of *p*-iodoethylbenzene in acetic acid, forms pale yellow needles decomposing at 103°, and when treated with 5 per cent. sodium hydroxide solution is converted into p-*iodosoethylbenzene*, which is an insoluble, white, amorphous powder melting at 89°.

p-Iodoxyethylbenzene, $C_6H_4Et \cdot IO_2$, is obtained from the chloride just described by prolonged treatment with concentrated sodium hypochlorite solution; it crystallises in white leaflets decomposing at 196·5°.

Di-p-*ethylphenyliodinium hydroxide* is obtained in aqueous solution by prolonged stirring of a mixture of molecular proportions of *p*-iodosoethylbenzene and *p*-iodoxyethylbenzene with moist silver oxide; the *chloride* crystallises in white needles melting at 150°, the *mercurichloride*, $I(C_6H_4Et)_2Cl,HgCl_2$, in needles melting at 120°, the *platinichloride* (with $3H_2O$) in yellow needles decomposing at 148°. The *bromide* forms needles which decompose when exposed to light, and melt at 145°; the *iodide* is unstable, and crystallises in needles melting at 42°.

Phenyl-p-*ethylphenyliodinium hydroxide* can be obtained as an aqueous solution in the usual manner; the *chloride* forms colourless stable needles melting at 169°, the *mercurichloride*,

$$(C_6H_4Et \cdot IPhCl)_2,HgCl_2,$$

needles melting at 125°, and the *platinichloride*, which crystallises with $3H_2O$, separates in yellow needles melting at 155°. The *bromide*

crystallises in needles melting at 172°, the *iodide* in yellow needles melting at 160°, and the *nitrate* in leaflets melting at 138°.

p-*Ethylphenyl*-o-*tolyliodinium hydroxide* was obtained in aqueous solution in the usual manner; the *chloride* crystallises in leaflets melting at 165°, the *platinichloride* forms yellow flocks melting at 132°, the *bromide* crystallises in leaflets melting at 150°, and the *iodide* is a white precipitate melting at 139°.

Monoiododi-p-*ethylphenyliodinium hydroxide*,

$$IC_6H_3Et\cdot I(C_6H_4Et)\cdot OH,$$

is obtained in solution by treating the iodide with moist silver oxide; a solution of the sulphate of this base is prepared by introducing moist *p*-iodosoethylbenzene into sulphuric acid, cooled to $-10°$, and then diluting with ice; the iodide is precipitated when potassium iodide is added to the solution of the sulphate; it melts at 90°. The *bromide* is obtained in a similar manner, and crystallises in white leaflets melting at 120°. A *mercurichloride*,

$$[C_6H_4Et\cdot I(C_6H_3IEt)Cl]_2,HgCl_2,$$

also prepared from the sulphate, crystallises in pale rose-coloured leaflets melting at 142°; the *platinichloride* forms yellow needles melting at 135°.

Dichloroethyl-p-*ethylphenyliodinium chloride*, $C_2H_3Cl_2\cdot I(C_6H_4Et)Cl$, is obtained when acetylene-silver chloride and *p*-ethylphenyl iodochloride are intimately mixed in the presence of water, and crystallises in needles, melting at 134°, and decomposing when exposed to light; the *mercurichloride*, $[C_2H_3Cl_2\cdot I(C_6H_4Et)Cl]_2HgCl_2$, crystallises in needles melting at 67·5°, and the *platinichloride* in yellow needles, with $2H_2O$, melting at 128°. The *bromide* forms needles melting at 129°, and the *iodide* a yellow, amorphous powder which is very unstable and decomposes at 69°.

p-*Ethylphenyl*-α-*naphthyliodinium hydroxide*, $C_6H_4Et\cdot I(C_{10}H_7)\cdot OH$, can be prepared in a moderately concentrated aqueous solution by treating an aqueous suspension of α-iodosonaphthalene and *p*-iodoxyethylbenzene with silver oxide; the *chloride* is a white powder melting at 168°, the *mercurichloride*, $[C_6H_4Et\cdot I(C_{10}H_7)Cl]_2,HgCl_2$, a white powder melting at 56°; the *platinichloride* crystallises in yellow needles melting at 170°. The *bromide* forms white flocks melting at 156°, and the *iodide* is a yellow powder melting at 48°; the *dichromate* is a very unstable yellow powder exploding at 56°. K. J. P. O.

Derivatives of *p*-Iodopropylbenzene containing Polyvalent Iodine. Conrad Willgerodt and Paul Sckerl (*Annalen*, 1903, **327**, 301—317).—p-*Aminopropylbenzene* is prepared by heating aniline (2 parts), *n*-propyl alcohol (1—2 parts), and zinc chloride (3 parts) at 280° in iron pressure tubes and fractionating the crude product; the base is purified by conversion into the sulphate, and is a colourless oil boiling at 224—226°. p-*Iodopropylbenzene* is prepared in the usual manner by diazotising the pure sulphate, and is a pale yellow oil boiling at 240—242° and having an aromatic odour.

p-*Iodosopropylbenzene*, $C_6H_4Pr^{\alpha}\cdot IO$, prepared from the chloride, is a white powder which explodes at 105°; the *chloride*, $C_6H_4Pr^{\alpha}\cdot ICl_2$, is prepared by passing chlorine into a solution of *p*-iodopropylbenzene

dissolved in a mixture of chloroform and petroleum, and crystallises in yellow needles melting at 68°. The *acetate*, $C_6H_4Pr^a{\cdot}I(OAc)_2$, crystallises in transparent prisms melting at 101°, and is unstable. The *basic nitrate*, $C_6H_4Pr^a{\cdot}I(OH){\cdot}NO_3$, is an unstable powder which decomposes, yielding an oil; the *basic sulphate*, $[C_6H_4Pr^a{\cdot}I(OH)]_2SO_4$, is a yellowish-white powder exploding at 90°, the *basic iodate* a yellow, crystalline powder decomposing at 75°, and the *basic perchlorate* a lemon-yellow powder which explodes with violence at 73°, and spontaneously on keeping. The *chromate* is a very unstable, pale red precipitate, which sinters at 30° and explodes violently at 35—40°.

p-*Iodoxypropylbenzene*, $C_6H_4Pr^a{\cdot}IO_2$, is most easily prepared by treating the corresponding iodoso-compound with cold water, and crystallises in leaflets which explode at 180—200°. Only an impure material can be prepared by the action of hypochlorous acid on the iodoso-derivative.

Di-p-*propylphenyliodinium hydroxide*, $I(C_6H_4Pr^a)_2{\cdot}OH$, can only be obtained in small quantity by Meyer and Hartmann's method, but can be more easily prepared by warming the iodoso-derivative with water containing silver oxide in suspension. Addition of sodium chloride, bromide, or iodide to the solution of the base brings about the precipitation of the corresponding salt. The *chloride* crystallises in colourless needles melting at 143°; the *mercurichloride*, $I(C_6H_4Pr^a)_2Cl,HgCl_2$, is a crystalline precipitate melting at 128°; the *platinichloride* forms flesh-coloured leaflets decomposing at 163°. The *bromide* crystallises in colourless needles melting at 158°, and the *iodide* in lustrous needles melting and decomposing at 135—140°; the *periodide*, $I(C_6H_4Pr^a)_2I_3$, is prepared by adding a solution of iodine in chloroform to a solution of the iodide in the same solvent and precipitating with petroleum; it forms lustrous crystals melting at 57°. The *iodate*, forms a yellow, transparent mass melting and decomposing at 92°.

p-*Propylphenyl*-o-*tolyliodinium hydroxide* is obtained in aqueous solution by shaking a mixture of *p*-iodoxypropylbenzene and *o*-iodosotoluene with silver oxide and water. The *chloride* crystallises in colourless leaflets melting and decomposing at 133°, the *platinichloride* in red forms melting and decomposing at 144°. The *bromide* is a crystalline powder melting and decomposing at 133°, and the *iodide* forms white crystals decomposing at 123°.

Monoiododi-p-*propylphenyliodinium hydroxide*,

$$C_6H_4Pr^a{\cdot}I(C_6H_3Pr^aI){\cdot}OH,$$

is prepared from the iodide. A solution of the *sulphate* is prepared by adding *p*-iodosopropylbenzene to sulphuric acid cooled to −8°. The *chloride* is unstable and melts and decomposes at 43°; the *mercurichloride*, $C_6H_4Pr^a{\cdot}I(C_6H_3Pr^aI)Cl,HgCl_2$, forms rosettes of crystals decomposing at 95°, the *platinichloride* a rose-coloured precipitate decomposing at 140°; the *bromide* is a white precipitate melting at 45°, and, like the chloride, decomposes on boiling with water, and the *iodide* decomposes at 38°.

The authors express the opinion that the action of sulphuric acid on iodoso-compounds does not produce, as Meyer believed, an alternate addition and elimination of water, but rather that the following series of changes take place: $IPhO + H_2SO_4 = IPh{:}SO_4 + H_2O$; $IPh{:}SO_4 +$

$H_2SO_4 = IPh(O\cdot SO_3H)_2$; then $2IPh(O\cdot SO_3H)_2 = C_6H_4I\cdot IPh\cdot O\cdot SO_3H + H_2SO_4 + H_2S_2O_8$; or $IPh{<}^{O}_{O}{>}SO_2 + IPh(O\cdot SO_3H)_2 =$

$$C_6H_4I\cdot IPh\cdot O\cdot SO_3H + H_2S_2O_8.$$

K. J. P. O.

Substitution of Oxygen by Fluorine in Iodoxy- and Iodoso-compounds. RUDOLF F. WEINLAND and W. STILLE (*Annalen*, 1903, 328, 132—139).—The replacement of oxygen by fluorine in aromatic iodoxy-compounds, which has been previously recorded (Abstr., 1901, i, 684), has been studied in several additional cases, and a number of iodosofluorides have been described. It has been also shown that in iodoso-compounds, oxygen can similarly be replaced by fluorine, iodofluorides being formed.

Toluene-m-*iodosofluoride*, $C_6H_4Me\cdot IOF_2$, is prepared by saturating warm 40 per cent. hydrofluoric acid with *m*-iodoxytoluene; on cooling, the iodosofluoride separates in small, colourless needles, melting, when rapidly heated, at 180°, and decomposing at 188°. *Bromobenzene*-p-*iodosofluoride*, $C_6H_4Br\cdot IOF_2$, crystallises in small needles exploding at 225°.

Tolyl p-*iodofluoride*, $C_6H_4Me\cdot IF_2$, is prepared by slowly adding hydrofluoric acid to a solution of *p*-iodosotoluene in acetic acid, when the iodofluoride slowly separates in small, yellow needles; this substance can only be obtained in a pure state when very small quantities are used and the temperature kept at 40°; it melts at 112° and decomposes at 115°. *Bromophenyl* p-*iodofluoride*, $C_6H_4Br\cdot IF_2$, prepared in a similar manner, crystallises in yellow needles melting at 110° and decomposing at 135—140°. K. J. P. O.

Action of Sulphur and of Selenium on Magnesium Phenyl and Magnesium α-Naphthyl Bromides. TABOURY (*Bull. Soc. chim.*, 1903, [iii], 29, 761—765).—Sulphur interacts with magnesium phenyl bromide in ethereal solution, and, on decomposing the product with dilute hydrochloric acid, thiophenol and phenyl disulphide are obtained; similarly, magnesium α-naphthyl bromide gives α-thionaphthol and naphthyl disulphide. Replacing the sulphur by selenium, selenophenol and α-selenonaphthol are formed. If, instead of decomposing the first product of the interaction of sulphur and the aryl magnesium bromide with dilute acid, benzoyl chloride is employed, the benzoates of thiophenol and α-thionaphthol are obtained; *phenyl thiolbenzoate*, $SPh\cdot COPh$, crystallises from dilute alcohol in needles and melts at 56°; *α-naphthyl thiolbenzoate*, $C_{10}H_7\cdot S\cdot COPh$, melts at 117—118°. W. A. D.

Asymmetric Tetramethyldiaminophenyldiphenylenemethane and a Colouring Matter derived from it. ALFRED GUYOT and M. GRANDERYE (*Compt. rend.*, 1903, 137, 413—414. Compare Haller and Guyot, Abstr., 1901, i, 569).—as-*Tetramethyldiaminophenyldiphenylenemethane* was obtained by dissolving the *o*-amino-leucobase of malachite green in sulphuric acid, diazotising at 0°, and then warming to 100°. It is obtained in slender, white crystals by precipitating a benzene solution with hot alcohol; it melts at 149° and

is very soluble in benzene. This leucobase, when oxidised, gives a violet colouring matter; the oxidation was carried out in hydrochloric acid solution with lead peroxide. The *hydrochloride*,

$$NMe_2{\cdot}C_6H_4{\cdot}CCl{<}\begin{matrix}C_6H_3{\cdot}NMe_2\\ |\\ C_6H_4\end{matrix},$$

is very soluble in hot water, and crystallises in long, slender, dark needles. With potassium or lead nitrate, it gives the corresponding *nitrate* in a similar form.

The salts are not substantive dyes, but give a violet shade on wool mordanted with aluminium or iron; they are not fluorescent.

J. McC.

Addition of Hydrogen Fluoride to Salts of Sulphonic Acids. RUDOLF F. WEINLAND and W. STILLE (*Annalen*, 1903, 328, 140—149).—The property possessed by hydrogen fluoride of forming crystalline additive products with the potassium, rubidium, and cæsium salts of various sulphonic acids has been previously described (Weinland and Kappeller, Abstr., 1901, i, 309). It is now found that the alkali salts (including the ammonium, lithium, and sodium compounds) of thymol-6-sulphonic acid exhibit this property to a remarkable degree. The presence of the corresponding alkali fluoride favours the separation of the additive product, and the ammonium salts of the sulphonic acids are also generally capable of forming these additive compounds when ammonium fluoride, as well as hydrofluoric acid, is added to the solution of the sulphonate.

Potassium thymolsulphonate forms the *additive* compound,

$$OH{\cdot}C_6H_2MePr_\beta{\cdot}SO_3K,2HF,$$

when potassium thymolsulphonate and excess of potassium fluoride are dissolved in warm 40 per cent. hydrofluoric acid and the mixture allowed slowly to concentrate over phosphoric oxide and alkali hydroxide; the salt separates in large, four-sided plates, which are not stable even in dry air. The *rubidium*, *cæsium*, and *ammonium* salts are isomorphous with the potassium salt. The *sodium* salt,

$$OH{\cdot}C_6H_2MePr^\beta{\cdot}SO_3Na,HF,$$

forms rectangular crystals. The *lithium* salt has a similar composition and closely resembles the sodium salt.

Ammonium benzenesulphonate and hydrofluoric acid form the *double* salt, $PhSO_3{\cdot}NH_4,HF$, which is very stable and crystallises in thin leaflets; the analogous *derivative* of ammonium *p*-phenolsulphonate, $OH{\cdot}C_6H_4{\cdot}SO_3{\cdot}NH_4$, is also stable and crystallises in thin leaflets. The *derivative* of ammonium sulphosalicylate,

$$SO_3NH_4{\cdot}C_6H_3(OH){\cdot}CO_2H,HF,$$

crystallises in leaflets and is very stable. The *double* salt, obtained from potassium di-iodo-*p*-phenolsulphonate, $OH{\cdot}C_6H_2I_2{\cdot}SO_3K,HF$, crystallises in needles; the *rubidium* and *ammonium* salts closely resemble it.

K. J. P. O.

Transition of Different Substituted Anilines into Compounds of the Ammonium Type. NICOLAI A. MENSCHUTKIN and L. SIMANOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 204—210. Compare Fischer and Windaus, Abstr., 1900, i, 224).—The author has

made a number of experiments on the combination of allyl haloid compounds with pyridine, α-picoline, diallyl-*o*-toluidine, dimethylaniline, dimethyl-*v*-*m*-xylidine, methylaniline, *o*- and *m*-toluidines and *m*-xylidine, from the results of which the following conclusions are drawn: tertiary anilines, and also the tertiary bases of the pyridine and quinoline groups with allyl bromide or iodide or methyl iodide, yield, besides compounds of the ammonium type, a certain proportion of the hydrogen-haloid salt of the base taken, varying with the conditions. For the tertiary anilines, the combined action of allyl and methyl iodides will not serve for showing that they contain a benzene nucleus. With 1 mol. of alkyl iodide, primary or secondary anilines give substituted aniline salts, but no quaternary ammonium compounds, and with an excess of the alkyl haloid this action also takes place, only to a greater extent. Conclusions regarding the influence of the side-chain, as evidenced by these results, must be drawn with caution.

The following new compounds were prepared by the action of 2 mols. of allyl iodide on 1 mol. of the corresponding toluidine in presence of sodium carbonate solution:

Diallyl-o-toluidine, $C_6H_4Me{\cdot}N(C_3H_5)_2$, boils at 229—232° and has a sp. gr. 0·9392 at 19°.

Diallyl-m-toluidine boils at 245—249° and has a sp. gr. 0·9430 at 19°.

Diallyl-p-toluidine boils at 252—257° and has the sp. gr. 0·9442 at 19°.

These compounds are all pale yellow oils with a characteristic aromatic odour; in the air, they turn brown and become tarry. They dissolve in acids, but the solutions do not give crystalline salts except in the case of the *picrates*, which form microscopic, yellowish-red, rhombic and hexagonal prisms and plates soluble in alcohol.

T. H. P.

Diphenamine [Dianilino-] Compounds of Aldehydes. ALEXANDER EIBNER (*Annalen*, 1903, 328, 121—131. Compare Abstr., 1899, i, 41; 1901, i, 97, 376, 640).—A *résumé* is given of recent work on additive derivatives of aldehydes with aromatic amines, in which is included nitrogenous substances resembling (1) the true aldehydic polymerides, (2) the aldol condensation products, (3) the additive products of aldehydes and sulphurous acid or disulphites, (4) the additive products with water, the nitrogen analogues of which are the dianilino-derivatives of aldehydes and aniline and its homologues,

$$R{\cdot}CH(NHPh)_2.$$

A more detailed account than that previously published of the characters of the dianilino-compounds is given, and various additional facts are recorded. Propaldehyde and aniline (2 mols.) yield an oily dianilino-compound. On oxidation, all dianilino-compounds yield azobenzene.

p-Chloroaniline (2 mols.) and *i*-valeraldehyde (1 mol.) yield a condensation product which forms needles or large prismatic crystals melting at 104°, and is not a dianilino-compound but a tertiary anhydrobase, $(C_5H_{10})_2(NH{\cdot}C_6H_4Cl)_2$; on reduction with sodium and alcohol,

p-chloro-*i*-amylaniline and an ethylene base of characteristic odour are formed.

i-Valeraldehyde and *p*-nitroaniline condense, on the other hand, forming a *dianilino*-compound, $C_5H_{10}(NH{\cdot}C_6H_4{\cdot}NO_2)_2$, which crystallises in yellow needles melting at 158°, and is readily hydrolysed by warm dilute sulphuric acid.

The aliphatic aldehydes, which are soluble in water, yield, with anilines, dianilino-derivatives, whilst those which are insoluble only yield these diamines with substituted anilines containing negative groups; in the absence of such groups, tertiary anhydro-compounds are formed. The aromatic aldehydes yield tertiary anhydro-bases with aniline and its homologues, even when these contain negative groups. K. J. P. O.

A Class of ψ-Thiocarbamides described as Normal Carbamides. Henry L. Wheeler and George S. Jamieson (*J. Amer. Chem. Soc.*, 1903, **25**, 719—722).—The alkyl derivatives of normal thiocarbamides have the alkyl group attached to sulphur, and, when further alkylation takes place, the substitution occurs at the nitrogen atom (Bertram, Abstr., 1892, 465). Certain thiocarbamides have, however, been described by Wunderlich (Abstr., 1886, 435) and by Hecht (Abstr., 1890, 476, 1103) as yielding nitrogen alkyl derivatives with alkyl haloids, but the authors now show that those compounds are ψ-thiocarbamides of the type $NR\colon C(SR'){\cdot}NH{\cdot}CN$, where the substituted alkyl group, R′, is attached to sulphur.

Cyanophenylmethyl-ψ-thiocarbamide, obtained by the action of methyl iodide on the crystalline product from sodium cyanoamide and phenylcarbimide (compare Hecht, *loc. cit.*), was heated with excess of alcoholic ammonia for five hours at 90—95°. Mercaptan was evolved, and *cyanophenylguanidine* was formed according to the equation $NPh\colon C(SMe){\cdot}NH{\cdot}CN + NH_3 = MeSH + NPh\colon C(NH_2){\cdot}NH{\cdot}CN$; it crystallises from alcohol in colourless needles melting at 190—191°. *Ammonium cyanophenylmethyl-ψ-thiocarbamide*, obtained by heating the ψ-thiocarbamide at 100° for five hours with alcoholic ammonia saturated with hydrogen sulphide, crystallises in colourless needles melting at about 142—143° to a pale yellow liquid.

Cyanophenylbenzyl-ψ-thiocarbamide, prepared according to Hecht's method, is identical with the substance obtained by Fromm (Abstr., 1895, i, 418). Both products melt at 182—183°, and yield identical methyl derivatives.

ψ-Thiocarbamides containing a –CN group are more stable and less chemically active than other ψ-thiocarbamides. They have acid properties and form salts with ammonia. A. McK.

ψ-Dithiobiurets. Treat B. Johnson (*Amer. Chem. J.*, 1903, **30**, 167—182).—Aqueous solutions of non-substituted ψ-thiocarbamides are fairly stable at the ordinary temperature (compare Wheeler and Merriam, this vol., i, 524) and readily combine with thiocarbimides to form a new class of ψ-dithiobiurets.

[With Howard S. Bristol.]—a-*Phenyl*-1-*methyl-ψ-dithiobiuret*, $NPh\colon C(SMe){\cdot}NH{\cdot}CS{\cdot}NH_2$, prepared according to Tursini's method

(Abstr., 1884, 1140), crystallises from alcohol in long prisms and melts at 122°. The corresponding ethyl compound, prepared by Tursini, differed in properties from the ψ-ethyldithiobiuret, NHPh·CS·N:C(SEt)·NH_2, prepared by the authors from ψ-ethylthiocarbamide and phenylthiocarbimide. The action of a thiocarbimide on a substituted ψ-thiocarbamide is represented by an equation such as SEt·C(NH_2):NPh + PhCNS = SEt·C(:NH)·NPh·CS·NHPh (labile) → SEt·C(:NPh)·NH·CS·NHPh (stable), although, however, no formation of labile products was observed in any instance.

a-*Phenyl*-2-*methyl*-ψ-*dithiobiuret*, NHPh·CS·NH·C(SMe):NH, prepared by the action at the ordinary temperature of phenylthiocarbimide on methyl-ψ-thiocarbamide, separates from alcohol in prisms which melt and decompose at 124°. Its melting point is lowered to 102° by admixture with *a*-phenyl-1-methyl-ψ-dithiobiuret. Instead of forming a triazole derivative with phenylhydrazine, phenylthiocarbimide is liberated and diphenylthiosemicarbazide is produced. The corresponding *ethyl* derivative forms yellow, tabular crystals and melts at 114°.

p-*Tolylmethyl*-ψ-*thiocarbamide hydriodide*, prepared from *p*-tolylthiocarbamide and methyl iodide, crystallises in prisms and melts and decomposes at 129—130°. The *base* separates from light petroleum in plates and melts at 65—67° (compare Dixon, Trans., 1903, **83**, 556).

c-*Phenyl*-a-p-*tolyl*-1-*methyl*-ψ-*dithiobiuret*,

C_6H_4Me·N:C(SMe)NH·CS·NHPh,

prepared from phenylthiocarbimide and *p*-tolylmethyl-ψ-thiocarbamide, crystallises from alcohol in prisms melting at 93°. With phenylhydrazine, it forms diphenylthiosemicarbazide. With methyl iodide, it forms c-*phenyl*-a-p-*tolyl*-1 : 2-*dimethyl*-ψ-*dithiobiuret hydriodide*, C_6H_4Me·N:C(SMe)·NH·C(SMe):NPh,HI, which crystallises from alcohol in prisms and melts at 164°; the base was obtained as an oil. a-p-*Tolyl*-a-b-*dimethyl*-ψ-*thiocarbamide hydriodide*,

C_7H_7·NMe·C(SMe):NH,HI,

prepared from methyl iodide and *p*-tolylmethyl-ψ-thiocarbamide, melts and decomposes at 190—191°; the free base was obtained as an oil. c-*Phenyl*-a-p-*tolyl*-2 : 1-*dimethyl*-ψ-*dithiobiuret*,

C_7H_7·NMe·C(SMe):N·CS·NHPh,

crystallises from alcohol in elongated prisms and melts at 124°; its *hydriodide* melts and decomposes at 182°.

[With Morgan S. Elmer.]—ac-*Diphenyl*-1-*methyl*-ψ-*dithiobiuret*, NPh:C(SMe)·NH·CS·NHPh, crystallises from alcohol in transparent prisms and melts at 101°. When warmed with hydrochloric acid, mercaptan is evolved and *methyl phenyldithioallophanate* is formed; this melts and decomposes at 157—158°. ac-*Diphenyl*-1 : 2-*dimethyl*-ψ-*dithiobiuret hydriodide*, NPh:C(SMe)NHC(SMe):NPh,HI, crystallises from alcohol in stout prisms, which melt and decompose at 154—155°. The *base* forms acicular prisms and melts at 103—104°. ac-*Diphenyl*-a-1-*dimethyl*-ψ-*dithiobiuret*, NMePh·C(SMe):N·CS·NHPh, crystallises from alcohol in stout prisms and melts at 133—134°. ac-*Diphenyl*-1-*benzyl*-ψ-*dithiobiuret*, NPh:C(S·C_7H_7)·NH·CS·NHPh, separates from alcohol in colourless prisms and melts at 98—100°.

Benzoylthiocarbimide acts violently on phenylbenzyl-ψ-thiocarbamide to form a substance which melts at 190—191° and which is probably a triazine derivative.

[With William B. Cramer.]—By the action of phenylthiocarbimide on *o*-tolylmethyl-ψ-thiocarbamide (m. p. 101°, compare Dixon, *loc. cit.*), c-*phenyl*-a-o-*tolyl*-1-*methyl-ψ-dithiobiuret*,

$$C_6H_4Me \cdot N⁚C(SMe) \cdot NH \cdot CS \cdot NHPh,$$

was formed; it crystallises from alcohol in plates and melts at 114—115°.

c-*Phenyl*-a-o-*tolyl*-1 : 2-*dimethyl-ψ-dithiobiuret hydriodide*,

$$C_6H_4Me \cdot N⁚C(SMe) \cdot NH \cdot C(SMe)⁚NPh,HI,$$

melts and decomposes at 147—148°; the *base* crystallises from alcohol in prisms and melts at 70—71°.

a-*Phenyl*-c-o-*tolyl*-1-*methyl-ψ-dithiobiuret*,

$$NPh⁚C(SMe) \cdot NH \cdot CS \cdot NH \cdot C_6H_4Me,$$

crystallises from alcohol in plates and melts at 114—115°. When its methyl iodide additive product is decomposed by sodium hydroxide, *a-o*-tolyl-*c*-phenyl-1 : 2-dimethyl-ψ-dithiobiuret is formed.

c-*Phenyl*-a-o-*tolyl*-1-*ethyl-ψ-dithiobiuret*,

$$C_6H_4Me \cdot N⁚C(SEt) \cdot NH \cdot CS \cdot NHPh,$$

crystallises from dilute alcohol in plates and melts at 117—118°. When heated with hydrochloric acid, mercaptan is evolved and ethyl phenyldithioallophanate is produced.

a-*Phenyl*-c-o-*tolyl*-1-*ethyl-ψ-dithiobiuret*,

$$NPh⁚C(SEt) \cdot NH \cdot CS \cdot NH \cdot C_6H_4Me,$$

crystallises from alcohol in plates and melts at 95—96°. ac-*Diphenyl*-1-*ethyl-ψ-dithiobiuret*, $NPh⁚C(SEt) \cdot NH \cdot CS \cdot NHPh$, crystallises from alcohol in plates and melts at 91—93°. ac-*Di*-o-*tolyl*-1-*ethyl-ψ-dithiobiuret*, $C_6H_4Me \cdot N⁚C(SEt) \cdot NH \cdot CS \cdot NH \cdot C_6H_4Me$, crystallises from alcohol in prisms and melts at 86—87°.

ac-*Di*-o-*tolyl*-1-*methyl-ψ-dithiobiuret*,

$$C_6H_4Me \cdot N⁚C(SMe) \cdot NH \cdot CS \cdot NH \cdot C_6H_4Me,$$

crystallises from alcohol in plates and melts at 122—123°.

A. McK.

Action of Alkali Sulphides on *p*-Nitrobenzylaniline. Frederick J. Alway and Arthur B. Walker (*Amer. Chem. J.*, 1903, **30**, 105—110).—*p*-Nitrobenzylaniline undergoes simultaneous oxidation and reduction when heated with alkali sulphides in alcoholic solution, *p*-aminobenzylideneaniline being formed (D.R.-P. 99542). If the proportion of sodium sulphide is not greater than 1 mol. to 8 mols. of nitrobenzylaniline, or if alkali hydroxides are employed, the principal product is *p*-azoxybenzylideneaniline. C. H. D.

Arylation of α-Aminonitriles. Badische Anilin- & Soda-Fabrik (D.R.-P. 142559).—α-Aminonitriles react with aromatic amines of the benzene series or their alkyl derivatives to form aryl derivatives: $X \cdot NH_2 + Ar \cdot NH_2 = X \cdot NHAr + NH_3$; $X \cdot NH_2 + Ar \cdot NHR = X \cdot NArR + NH_3$. The reaction takes place readily between the free substances or their salts in aqueous or alcoholic solution at the

temperature of the water-bath. *Anilinoacetonitrile*, $NHPh\cdot CH_2\cdot CN$, from aminoacetonitrile hydrochloride and aniline, separates from ether in colourless crystals melting at 43°. *Ethylanilinoacetonitrile*, $NPhEt\cdot CH_2\cdot CN$, is a colourless oil boiling at 183° under 20 mm. pressure, and solidifying when cooled to large, colourless crystals melting at 24°, converted by heating with concentrated sulphuric acid into the *amide*, $NPhEt\cdot CH_2\cdot CO\cdot NH_2$, melting at 114°. *α-Anilinopropionitrile*, $NHPh\cdot C_2H_4\cdot CN$, melts at 92°. C. H. D.

Preparation of Phenylglycine-*o*-carboxylic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 142506 and 142507. Compare Abstr., 1902, i, 367).—Phenylglycine-*o*-carboxylic acid is obtained almost quantitatively by boiling the alkali salts of *o*-chlorobenzoic acid and glycine with potassium carbonate solution for 4—6 hours. If copper salts or copper turnings be added, the time required is only 1—1½ hours. C. H. D.

Substituted Derivatives of Ethyl Anilinomalonate. Richard Sydney Curtiss (*Amer. Chem. J.*, 1903, 30, 133—144).—Ethyl anilinomalonate reacts with nitrous acid forming a nitroso-derivative, $NO\cdot NPh\cdot CH(CO_2Et)_2$ or $OH\cdot N_2Ph\colon C(CO_2Et)_2$ (compare Abstr., 1900, i, 482). The corresponding toluidino-compounds have now been investigated. *Ethyl* o-*toluidinomalonate*, $C_6H_4Me\cdot NH\cdot CH(CO_2Et)_2$, prepared from *o*-toluidine and ethyl bromomalonate, is a colourless oil, which reduces an ammoniacal solution of silver nitrate; its *hydrochloride* forms white crystals which melt at 87—90°. Nitrous acid converts it into a viscous, uncrystallisable oil, which gives the Liebermann nitroso-reaction. *Ethyl* m-*toluidinomalonate* crystallises from light petroleum or absolute alcohol in colourless needles melting at 50·5—51°. The *hydrochloride* crystallises from alcohol or ether in rosettes of silky needles melting at 80—83°, and the *nitroso*-compound forms pinkish-amber prisms melting at 58—58·5°. Ethyl *p*-toluidinomalonate has been described by Blank (Abstr., 1898, i, 589); its *nitroso*-compound is a viscous oil which crystallises with great difficulty. C. H. D.

Dependence of the Acidity of Phenols on their Composition and Structure. Paul N. Raikow (*Chem. Zeit.*, 1903, 27, 781—788. Compare this vol., i, 162).—The author has studied the relative strengths of a large number of substituted phenols by observing their ability either to combine with ammonia or to decompose the following series of salts: sodium silicate, potassium carbonate, hydrogen carbonate, phosphate, hydrogen phosphate, dihydrogen phosphate, pyrophosphate, metaphosphate, ferrocyanide, ferricyanide, sulphite, sulphate, hydrogen sulphate, borate, and nitrite. The following summary of the results is given. The introduction of an alkyl group into the molecule of a phenol usually diminishes the acidity (*o*- and *m*-cresols, carvacrol, methylcresol, trinitrocresol), but the reverse obtains in some cases, *p*-cresol for instance; the introduction of propylene (eugenol) increases the acidity. The polyhydric phenols are

usually much stronger acids than phenol, but there is little difference as regards acidity between di- and tri-hydric compounds; phloroglucinol is remarkable for being only slightly acid as compared with the isomeric pyrogallol. The increase of acidity caused by hydroxyl is still recognisable when this radicle is present in the side-chain (saligenol), and a sulphydryl group has the same influence as hydroxyl; the action of a methoxyl group is less acidifying than hydroxyl (guaiacol, catechol, and vanillin). The aldehydic group CHO distinctly enhances the acidity of a phenol. The influence of the group CO_2R depends on the chemical nature and molecular magnitude of the alkyl radicle R, and also on the relative position of the hydroxyl and carbalkoxyl groups. Under similar conditions, an alkyl radicle diminishes the acidity of a phenol more than a phenyl group, this difference being exemplified in the case of methyl, ethyl, and phenyl salicylates, and the higher alkyl group has the greater effect. When the radicle CO_2R is in the ortho-position relatively to hydroxyl, the acidity is always decreased, so that methyl and ethyl salicylates and the esters of the three *o*-hydroxytoluic acids (Me = 3, 4, or 5) are weaker than phenol; when, however, the ester radicle is in the meta-position, the acidity is slightly increased (methyl *m*-hydroxybenzoate), whilst when it is in the *p*-position the increase of acidity is the same as that caused by the addition of another hydroxyl group (methyl *p*-hydroxybenzoate, methyl vanillate, guaiacol). Iodine and bromine as a rule increase the acidity, the influence of iodine being less than that of bromine, but iodophenol is exceptional, being less acid than phenol. Contrary to expectation, the amino-group invariably increases acidity, whether it is present in the nucleus (aminophenols) or as an acid amide (salicylamide). The nitro-group is very strongly acidifying, *p*-nitrophenol, for instance, being a stronger acid than tribromophenol, whilst picric acid can remove potassium from potassium sulphate, although not able to decompose potassium hydrogen sulphate or the corresponding dihydrogen phosphate. W. A. D.

Solubility of Picric Acid in Ether. J. Bougault (*J. Pharm. Chim.*, 1903, [vi], 18, 116—117).—A specimen of "dry" ether (sp. gr. 0·721), previously washed with water and dried over calcium chloride, dissolved 10·8 grams of picric acid per litre at 13°. The solubility of the acid in "wet" ether increases with the quantity of water present, thus ether of sp. gr. 0·725 and containing 0·8 per cent. of water dissolved 36·8 grams of picric acid per litre, whilst a third specimen of sp. gr. 0·726, containing 1 per cent. of water, dissolved 40 grams of the acid per litre. A solution of picric acid in dry ether (sp. gr. 0·720) is colourless, but becomes yellow on the addition of a minute quantity of water, the maximum intensity of coloration being reached when the sp. gr. of the ether has been raised to 0·725. This peculiarity, which it is suggested is due to the formation of a yellow hydrate of picric acid, may be used between the limits mentioned as a test for the amount of moisture present in commercial ether.

T. A. H.

Action of Nitric Acid on Halogen Derivatives of *p*-Alkylphenols. I. Chloro-derivatives of *p*-Cresol and their Behaviour towards Nitric Acid. THEODOR ZINCKE [with W. SCHNEIDER and WILHELM EMMERICH] (*Annalen*, 1903, **328**, 261—321. Compare Abstr., 1901, i, 330).—Nitric acid converts 3-chloro-*p*-cresol into 3-chloro-5-nitro-*p*-cresol, and then into a chloronitro-*p*-toluquinone, the methyl group having migrated to the neighbouring carbon atom, thus:

$$CMe{<}{\substack{CH{=}CCl \\ CH{\cdot}C(NO_2)}}{>}C{\cdot}OH \longrightarrow CO{<}{\substack{CMe{=}CCl \\ CH{:}C(NO_2)}}{>}CO.$$

3:5-Dichloro-, trichloro-, and tetrachloro-*p*-cresols, on the other hand, do not yield nitro-derivatives, in which a hydrogen atom of one of the CH groups has been substituted, but unstable quinone derivatives, thus: $NO_2{\cdot}CMe{<}{\substack{CH{:}CCl \\ CH{:}CCl}}{>}CO$; for these compounds, the name quinonitrole ("chinitrol") is suggested (compare Auwers, Abstr., 1897, i, 336).

3-Chloro-*p*-cresol is best prepared by passing the requisite amount of chlorine into a cold solution of *p*-cresol in carbon tetrachloride and fractionating the residue left on evaporation of the solvent; the fraction boiling at 190—200° is freed from *p*-cresol by shaking with concentrated sulphuric acid.

3:5-Dichloro-*p*-cresol (m. p. 39°) is prepared in an exactly similar manner from *p*-cresol; the *acetyl* derivative crystallises in leaflets melting at 48°, and the *benzoyl* derivative in plates melting at 91°.

2:3:5-*Trichloro*-p-*cresol* is prepared by passing chlorine into a solution of *p*-cresol in acetic acid until the solution smells of chlorine; in the course of 24 hours, the trichloro-compound separates in lustrous needles melting at 66—67°; it is also formed in the reduction of the heptachloroketochloride and the tetrachloroketochloride; the *acetyl* derivative crystallises in needles melting at 37—38°, and the *benzoyl* derivative in plates melting at 89°.

2:3:5:6-*Tetrachloro*-p-*cresol* is only obtained by reducing the pentachloroketochloride, which is produced in an impure state by adding potassium acetate to an acetic acid solution of the heptachloride; it crystallises in long, white needles melting at 190°, and on treatment with chlorine in acetic acid solution is converted into pentachloroketochloride; the *acetyl* derivative crystallises in needles or leaflets melting at 112°.

Tetrachloroketodihydrotoluene (*tetrachloro*-p-*cresolketochloride*),

$$CMe{<}{\substack{CH{=}CCl \\ CCl{\cdot}CCl_2}}{>}CO,$$

is prepared either by passing chlorine into a suspension of trichloro-*p*-cresol in acetic acid or by adding bleaching powder solution to an acetic acid solution of the same trichloro-compound; it forms prismatic crystals from benzene melting at 106—107°, is insoluble in alkalis, and sets free iodine from potassium iodide; on reduction, it is reconverted into trichlorocresol. *Pentachloroketodihydrotoluene* (*pentachloro*-p-*cresolketochloride*), $CMe{<}{\substack{CCl{\cdot}CCl_2 \\ CCl{=}CCl}}{>}CO$, is best prepared by adding potassium acetate to a suspension of the heptachloroketochloride in acetic acid, when the ketochloride dissolves; it can also be

obtained by the action of chlorine or hypochlorous acid on tetrachloro-*p*-cresol; it crystallises in large, monoclinic prisms melting at 99—100°, slowly dissolves in alkalis forming tetrachlorocresol, and is readily reduced to the same compound.

Heptachloroketohexahydrotoluene (*heptachloro-p-cresolketochloride*),

$$CMeCl<\begin{matrix}CHCl\cdot CCl_2\\CHCl\cdot CCl_2\end{matrix}>CO,$$

is prepared by passing a stream of moist chlorine through a suspension of moist *p*-toluidine hydrochloride in acetic acid containing hydrochloric acid until the liquid is saturated; the ammonium chloride is filtered off and the acetic acid evaporated at the ordinary temperature; the heptachloride forms large, monoclinic crystals, often prisms, melting at 110°, and is reduced by stannous chloride to a mixture of di- and tri-chloro-*p*-cresols.

On passing chlorine into a solution of *p*-cresol in carbon tetrachloride in the presence of iron, a ketochloride, $C_7H_2OCl_8$, was obtained in crystals melting at 168°, and easily reduced to chlorocresols by stannous chloride.

2 : 6-*Dichloromethylbenzoquinonitrole*, $NO_2\cdot CMe<\begin{matrix}CH:CCl\\CH:CCl\end{matrix}>CO$, is readily prepared by adding 1 c.c. of nitric acid of sp. gr. 1·5 to a solution of 1 gram of 3 : 5-dichloro-*p*-cresol in 5 grams of acetic acid, and then slowly introducing cold water, when the quinonitrole separates in lustrous needles, which become red on heating and melt and decompose at 74—76°; the solution of this substance in all solvents soon decomposes, nitrous fumes being formed; even in the dry state it decomposes within 24 hours, a red tar being formed which contains much chloronitrocresol. In solution in acetic acid, it is converted into dichloromethyl-*ψ*-quinol, and dichlorocresol is regenerated both by reducing agents and by alkalis. A *substance* which is free from nitrogen and crystallises in prisms or plates melting and decomposing at 154—155°, is produced together with methyl nitrite when the quinonitrole is warmed with methyl alcohol.

2 : 3 : 6-*Trichloromethylbenzoquinonitrole*, $NO_2\cdot CMe<\begin{matrix}CCl:CCl\\CH:CCl\end{matrix}>CO$, readily prepared in the same manner as the last-mentioned compound, forms colourless crystals, becoming red at 65° and melting and decomposing at 70°; it is readily converted into the corresponding *ψ*-quinol and into the original trichlorocresol. On warming with methyl alcohol, methyl nitrite is produced, together with a substance which crystallises in colourless prisms and melts at 203—204° evolving a slight amount of gas.

2 : 3 : 5 : 6-*Tetrachloromethylbenzoquinonitrole* crystallises in monoclinic prisms which become red at 80° and melt and decompose at 90°; it closely resembles the two substances just described, and yields the corresponding *ψ*-quinol when kept in acetic acid solution. When the solid is warmed with methyl or ethyl alcohol, the prisms of the quinonitrole change into the needles of a substance which is probably *tetrachloromethylenebenzoquinone*, $CH_2:C<\begin{matrix}CCl:CCl\\CCl:CCl\end{matrix}>CO$; it is pale yellow in colour, becomes white at 100°, sinters at 200°, but does not

melt at 270°; it is insoluble in alkalis, but dissolves in chloroform, &c., with an intense yellow coloration, a colourless decomposition product being slowly deposited. It is reduced by stannous chloride to tetrachlorocresol. When heated with methyl alcohol, it is converted into tetrachloro-*p*-hydroxybenzyl methyl ether (Abstr., 1902, i, 283); the corresponding *ethyl ether*, which is obtained in a similar manner, crystallises in long, white needles melting at 128°. By acetic acid, it is converted into the *acetyl* derivative (m. p. 170°),

$$OAc{\cdot}CH_2{\cdot}CH{<}{\scriptstyle CCl:CCl \atop CCl:CCl}{>}CO, \text{ or } OAc{\cdot}CH_2{\cdot}C{<}{\scriptstyle CCl:CCl \atop CCl\cdot CCl}{>}C{\cdot}OH$$

(*loc. cit.*). It dissolves in fuming nitric acid, the original quinonitrole being regenerated. Hydrogen bromide does not convert the quinone into a pseudobromide, but into tetrachloro-*p*-cresol.

2 : 6-*Dichloromethyl-ψ-quinol*, $OH{\cdot}CMe{<}{\scriptstyle CH:CCl \atop CH:CCl}{>}CO$, is prepared by shaking a suspension of the corresponding quinonitrole in acetic acid at the ordinary temperature until a red solution is obtained, the solvent is then partly evaporated, and the ψ-quinol precipitated by water; it crystallises from a mixture of petroleum and benzene in long needles, and from the latter solvent alone in monoclinic plates; it melts at 123°. Its solution in alkalis rapidly becomes coloured, the ψ-quinol decomposing; when reduced, dichlorocresol is regenerated. The *acetyl* derivative forms large crystals melting at 82—84°. 2 : 3 : 6-*Trichloromethyl-ψ-quinol* is prepared in the same manner as the compound last mentioned, but can also be readily obtained directly from trichloro-*p*-cresol by the action of nitric acid in acetic acid solution. After 24 hours, the solvent is evaporated at the ordinary temperature; the product crystallises from methyl alcohol in monoclinic plates and from petroleum in needles melting at 89—90°; the *acetyl* derivative crystallises in needles melting at 85—86°. 2 : 3 : 5 : 6-*Tetrachloromethyl-ψ-quinol* is prepared from the corresponding quinonitrole, or more simply by dissolving tetrachloro-*p*-cresol in hot nitric acid (sp. gr. 1·35); on cooling, the major part of the ψ-quinol crystallises out in long needles melting at 166°; it is soluble in alkali hydroxides unchanged, and is converted by concentrated sulphuric acid into the same condensation product (white needles, melting at 280° and soluble in alkalis) as is formed from tetrachloro-*p*-hydroxybenzyl alcohol. The *acetyl* derivative forms needles or leaflets melting at 135°. Amines react with the ψ-quinol; in the case of aniline, a mixture of anilides is formed when the reaction is carried out in alcoholic solution, but in benzene the *anilide*, $NHPh{\cdot}C_6Cl_3Me(OH){:}O$, is produced; this substance crystallises in pale yellow needles melting at 192°, and is soluble both in solutions of the alkali hydroxides and in concentrated sulphuric acid. When a solution of the ψ-quinol in alkali, the latter not being in excess, is kept for several hours, one atom of chlorine is replaced by hydroxyl, 2 : 3 : 5-*trichloro*-6-*hydroxymethyl-ψ-quinol* being formed, $OH{\cdot}CMe{<}{\scriptstyle C(OH):CCl \atop CCl=CCl}{>}CO$; this substance crystallises in needles with H_2O, changing at 110° and melting at 125°; it is reduced to trichloromethylresorcinol, and is converted by chlorine into a keto-

chloride: the *acetyl* derivative, $OH\cdot C_6Cl_3Me\cdot OAc$, crystallises in lustrous prisms melting and decomposing at 161°. When chlorine is passed into a solution of the hydroxy-ψ-quinol in acetic acid, a *compound*, $O\colon C_6Cl_3Me(OH)\colon O,H_2O$, which is at the same time a ψ-quinol and a ketochloride, is formed; it melts and loses water at 97°, melting when anhydrous at 103°. 2 : 3 : 6-*Trichloro-4-methylresorcinol*, $CMe\lessdot{}^{C(OH)\colon CCl}_{CCl\text{——}CCl}\gtrdot C\cdot OH$, is obtained on reduction of the hydroxy-ψ-quinol, and crystallises in needles melting at 134°, and is soluble in water; the *diacetyl* derivative forms colourless prisms melting at 126°.

Pentachloro-1 : 3-*diketo-4-methyltetrahydrobenzene* (*pentamethylresorcinoldiketochloride*), $CMe\lessdot{}^{CO-CCl_2}_{CCl\cdot CCl_2}\gtrdot CO$, prepared by saturating a solution of trichloromethylresorcinol in acetic acid with chlorine, forms large, colourless, monoclinic crystals melting at 85°. When treated in acetic acid solution with sodium acetate, the ring is broken, an acid, $C_7H_5O_3Cl_5$, being produced; this acid, which is probably a δ-ketonic acid, crystallises in needles melting at 115°, and is decomposed when its alkaline solution is heated. If bleaching powder is added to a solution of the ketochloride, another δ-ketonic acid, $C_7H_4O_3Cl_6$, is produced, forming rhombic prisms which melt at 133°; since this acid, under the influence of alkalis, yields chloroform, it contains the group $CCl_3\cdot CO\cdot$.

3-*Chloro-5-nitro*-p-*cresol*, prepared either by adding nitric acid of sp. gr. 1·4 to a solution of 3-chlorocresol in acetic acid or by adding excess of sodium nitrite to such a solution, crystallises in golden-yellow, flattened needles melting at 65°; the *sodium* salt forms red needles, the *barium* salt a red, the *silver* salt a reddish-brown, and the *lead* salt a yellow precipitate. The *methyl ether*, prepared from the silver salt, forms slender, yellow needles melting at 40—41°; the *acetyl* derivative crystallises in yellow needles melting at 95°. 3-*Chloro-5-amino*-p-*cresol*, prepared from the nitro-compound, crystallises in needles melting at 89—90°, soluble in alkali with a brown coloration; the *hydrochloride* crystallises in leaflets, and the *diacetyl* compound in needles melting at 162—163°. On subjecting the amino-compound to the action of chlorine, a *diketochloride*, $O\colon C_6Cl_5Me\colon O$, melting at 90°, is produced, which on reduction yields an o-*dihydroxybenzene* derivative melting at 179°.

Nitric acid converts 3-chlorocresol or the nitro-derivative just described into a nitrochloro-p-toluquinone (*loc. cit.*), which reacts with aniline yielding a *substance* crystallising in dark red leaflets, melting and decomposing at 260°. *Nitrochloro*-p-*toluquinol*,

$$OH\cdot C\lessdot{}^{CMe\colon C(NO_2)}_{CH\text{———}CCl}\gtrdot C\cdot OH \quad \text{or} \quad OH\cdot C\lessdot{}^{CH\cdot C(NO_2)}_{CMe=CCl}\gtrdot C\cdot OH,$$

is prepared by reducing the corresponding quinone with hydriodic acid, and crystallises in yellow needles melting at 179—180°, forming a dark liquid; it dissolves in alkalis with a dark red coloration; the *diacetyl* derivative forms aggregates of small prisms melting at 105—107°. The corresponding aminotoluquinol has been previously

described (*loc. cit.*); when a solution of the hydrochloride is treated with ferric chloride, a dark colour appears and a black substance separates; this substance, which is an o-*iminoquinone*,

$$OH\cdot C{<}{{CMe=CCl}\atop{CH\cdot C(:NH)}}{>}CO,$$

crystallises in black needles or prisms, is soluble in alcohol, forming an amethyst solution, and dissolves in concentrated sulphuric acid to a blue solution; alkalis cause the liberation of ammonia, and reducing agents the production of the original aminotoluquinol.

Trichlorotriketomethyltetrahydrobenzene, $CO{<}{{CMe:CCl}\atop{CCl_2-CO}}{>}CO,2H_2O$, is prepared by the prolonged treatment with chlorine of the hydrochloride of the aminotoluquinol suspended in acetic acid; ammonium chloride separates, and, on the addition of dilute hydrochloric acid, the ketochloride separates, which crystallises in rosettes of needles melting at 77—78°; alkalis rapidly attack this compound, dissolving and decomposing it. On reduction, it is converted into a very unstable *dichlorohydroxymethylquinol*, which crystallises in needles melting at 77—78°, dissolves in alkalis to a blue solution, and is rapidly oxidised by the air. On treating the acetic acid solution with nitric acid, *dichlorohydroxy*-p-*toluquinone*, $CO{<}{{CMe=CCl}\atop{CCl:C(OH)}}{>}CO$, is formed; it crystallises in pale red needles melting at 157—158°, and develops a bluish-violet coloration in sodium carbonate solution or in dilute aqueous caustic soda, but forms a colourless solution when the latter is concentrated. K. J. P. O.

Esterification of Unsymmetrical Di- and Poly-basic Acids. X. Phenylsuccinic Acid and its Esterification. RUDOLF WEGSCHEIDER and JOSEF HECHT (*Monatsh.*, 1903, 24, 413—433. Compare Abstr., 1903, i, 342).—When recrystallised from ether, light petroleum, or xylene by evaporation at the ordinary temperature, phenylsuccinic anhydride melts at 53°; when recrystallised from xylene, the temperature being maintained over 100°, it melts at 150° (compare Bredt and Kallen, Abstr., 1897, i, 155). After melting, it resolidifies in the more fusible form.

Phenylsuccinimide, produced by distilling the ammonium salt, crystallises in hard, white, short prisms, melts at 90°, and is soluble in alcohol, acetone, chloroform, or glacial acetic acid. *Potassium hydrogen phenylsuccinate*, $C_{10}H_9O_4K,H_2O$, crystallises in transparent, thick plates which lose H_2O on exposure to air. A silver hydrogen salt could not be obtained.

The *dimethyl* ester, $C_{10}H_8O_4Me_2$, obtained by the action of hydrogen chloride and methyl alcohol on the acid, crystallises in prisms, melts at 57°, and is easily soluble in methyl alcohol, chloroform, benzene, or acetone.

The a-*methyl* ester, $CO_2Me\cdot CHPh\cdot CH_2\cdot CO_2H$, obtained on partially hydrolysing the dimethyl ester by means of potassium hydroxide, crystallises in small prisms, melts at 102°, and is easily soluble in methyl alcohol, acetone, benzene, or chloroform.

The b-*methyl* ester, $CO_2H\cdot CHPh\cdot CH_2\cdot CO_2Me$, which is obtained

either by boiling the acid with methyl alcohol or, along with the dimethyl ester, on esterification of the acid with methyl alcohol and hydrogen chloride, forms feathery crystals, melts at 92° (Hahn, Dissertation, gives m. p. 74°), and is more easily soluble than the *a*-ester. The action of methyl alcohol or of sodium methoxide on the anhydride leads to the formation of a mixture of the two acid esters from which only a small amount of the *b*-methyl ester could be isolated.

When neutralised with ammonia, the acid esters give white, crystalline precipitates with silver nitrate, white, flocculent precipitates with lead acetate, brown and green precipitates with ferric and ferrous salts, and green and red colorations with nickel and cobalt salts respectively.

With $\mu_{\infty} = 374$, phenylsuccinic acid has a conductivity K 0·0160, the *a*-methyl ester K 0·0049, and the *b*-methyl ester K 0·0109.

G. Y.

Constitution of the Colouring Matters of Indigo. LOUIS MAILLARD (*Bull. Soc. chim.*, 1903, [iii], 29, 756—761. Compare Abstr., 1902, i, 371).—A theoretical paper in which it is suggested that indigotin and indirubin are stereoisomeric, being formed by the polymerisation of a substance, *hemi-indigotin*, to which is attributed Baeyer's formula for indigotin. According to this view, the final products have the following constitution:

$$\begin{array}{c} C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C\cdot C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4 \\ \quad\ |\quad | \\ C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C\cdot C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4 \end{array} \qquad \text{Indigotin.}$$

$$\begin{array}{c} C_6H_4<\begin{matrix}NH\\CO\end{matrix}>C\cdot C<\begin{matrix}NH\\CO\end{matrix}>C_6H_4 \\ \quad\ |\quad | \\ C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C\cdot C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4 \end{array} \qquad \text{Indirubin.}$$

W. A. D.

Mononitro-*o*-phthalic Acids. MARSTON T. BOGERT and L. BOROSCHEK (*J. Amer. Chem. Soc.*, 1903, 25, 767—770).—In connection with their work on derivatives of 3- and 4-nitrophthalic acids (Abstr., 1902, i, 98), the authors had omitted to consider the publications of Levi (*Inaug. Diss., Freiberg, i.B.*, 1891) and of Koch (*Inaug. Diss., Giessen*, 1900).

A. McK.

Combination of Bismuth with Tannic Acid. PAUL THIBAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 747—752. Compare this vol., i, 633).—Although anhydrous bismuth oxide does not combine with tannic acid, the hydrated oxides interact with an excess of the acid to form *bismuthotannic acid*, $(C_{14}H_9O_9)_3Bi_2,6H_2O$ or

$$C_{14}H_9O_{10}Bi,\tfrac{1}{2}(C_{14}H_{10}O_9),4H_2O.$$

The product is a yellow, amorphous powder which decomposes at 200—210° and dissolves in alkalis forming salts; the *sodium* salt, $(C_{14}H_6O_9)_3Bi_2Na_{12},4H_2O$, is precipitated from its solution by alcohol as a yellow, amorphous powder. When bismuth hydroxide is left suspended in a solution of tannic acid until it first becomes completely soluble in alkali, the product has the composition

$$C_{14}H_9O_{10}Bi,\tfrac{1}{4}(C_{14}H_{10}O_9),\tfrac{3}{2}H_2O;$$

the same substance is obtained by using pure digallic acid instead of tannic acid. When the tannic acid and bismuth hydroxide are brought together in water in theoretical proportions, the *compound* $C_{14}H_9O_{10}Bi,9H_2O$ is obtained; as it gives with aniline gallanilide and an *aniline bismuthogallate*, the structure of this compound is probably

$$C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(CO_2H){<}{}^{O}_{O}{>}Bi\cdot OH$$

or $C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)(CO_2H)\cdot O\cdot BiO$ (compare Sieker, *Jahresb. Pharm.*, 1896, 428). W. A. D.

Compounds from Lichens. Wilhelm Zopf (*Annalen*, 1903, 327, 317—354).—*Acarospora chlorophana* (*Pleopsidium chlorophanum*; *Lecanora flava β chlorophana*) contains, as was previously shown (Abstr., 1895, i, 297; *ibid.*, 1902, i, 465, 788), pleopsidic acid, together with rhizocarpic acid; the former acid has now been isolated in greater quantity from material collected in the Oetzthaler Alps. Pleopsidic acid crystallises in tetragonal pyramids melting at 131—132°, and not at 144—145° as previously recorded, and having $[\alpha]_D$ −55° to 60° at 18°; the analyses of the silver salt and the molecular weight determination by alkalimetry both point to the formula $C_{17}H_{28}O_4$. It is oxidised immediately by alkaline potassium permanganate solution, and when heated with absolute alcohol under pressure at 150—160° is partially converted into a substance which crystallises in scales melting at 43° and is insoluble in aqueous alkali hydroxides.

The substance, diffusin (m. p. 135°), which was isolated from *Parmelia diffusa* (Abstr., 1899, i, 716), has the formula $C_{31}H_{38}O_{10}$, melts at 135°, and reduces alkaline permanganate immediately.

d-Usnic acid, sordidin, and zeorin, which were found in the lichen *Lecanora sulphurea* (*Parmelia sordida β sulphurea*; *Lecanora polytropa* var. *sulphurea*; *Zeora sulphurea*), growing on granitic masonry in East Friesland (Abstr., 1895, i, 388), have now been obtained from specimens taken from a sandstone castle wall in Westphalia; from these, about 2 per cent. of usnic acid, $1\frac{1}{2}$ per cent. of sordidin, and far smaller quantities of zeorin were isolated.

In sterile specimens of *Usnea hirta* (*Usnea barbata forma hirta*), 3 per cent. of *d*-usnic acid, together with a very small quantity of a bitter principal, which appeared to be alectoric acid, were found; further, an acid was isolated which is found in no other *Usneæ*, and appears to be related to the fatty acids found in lichens; it is called *hirtic acid*, and crystallises in rhombic leaflets melting at 98°, and immediately reduces permanganate in the cold, but does not affect Fehling's solution. Fertile specimens of the same lichen also contain considerable quantities of usnic acid (3·1 per cent.), and very small amounts of atranoric, hirtic, and alectoric acids. By repeated extraction of *Usnea hirta* with much ether, a new acid, *hirtellic acid*, can be isolated, crystallising in four-sided prisms melting and decomposing at 215°; the alcoholic solution gives a wine-red coloration with traces of ferric chloride, and the alkaline solution immediately reduces permanganate in the cold.

Cladonia strepsilis (*C. polybotrya*) contains besides thamnolic acid a hitherto unrecognised product, *strepsilin*, which is of neutral character, and is probably a quinol derivative related to Hesse's pulveraric acid, since both substances give a green coloration with bleaching powder solution, a succession of colour changes (yellow, green, and blue) with concentrated sulphuric acid, and a blue colour with alcoholic ferric chloride.

Cladina destricta yields, in addition to *l*-usnic acid, an indigo, blue, insoluble substance, *destrictic acid*, related to, but not identical with, coccellic acid, found in *C. amaurocræa*; it is not found in the nearly related species, *C. amaurocræa* and *C. uncialis*, and in all probability the blue or bluish-green colour of *C. destricta* is due to the presence of this acid in a finely divided state in the superficial layers of the lichen.

Rhizonic acid was extracted by boiling ether from specimens of *Cladonia macilenta*, which were collected in the Arlberg (Tyrol); it was obtained as an ochre-yellow, crystalline mass or in colourless crystals (Hesse, Abstr., 1899, i, 381).

On extraction with ether, specimens of *Lecanora glaucoma* (*L. sordida α-glaucoma*, *Zeora sordida α-glaucoma*), also collected in the Tyrol, were found to contain atranoric, thiophanic, and roccellic acids. The yield of the last mentioned represents 3 per cent. of the dried lichen, whilst the others are present in far smaller amount. Specimens of this *Lecanora*, growing in low lying localities, such as the North German plains, contain only 0·9 per cent. of roccellic acid, no thiophanic acid, but 1·3 per cent. of atranoric acid; they yield, however, a substance which crystallises in colourless prisms and dissolves in aqueous potassium hydroxide with an intense yellow coloration.

Since the zeoric acid extracted from *Lecanora* (*Zeora*) *sordida* contains a higher percentage of hydrogen than parellic (psoromic) acid, and has at the same time a melting point which after several recrystallisations is not higher than 236°, it seems probable that Hesse's suggestion that zeoric acid is identical with these two acids is incorrect.

In a previous paper (Abstr., 1902, i, 465), it was stated that four substances were isolated from *Hæmatomma leiphæmum*, namely, atranoric acid, zeorin, leiphæmin, and a crystalline material; the leiphæmin has now been obtained quite free from zeorin, its melting point being 165—166°.

The crystalline material just mentioned has also been isolated in greater quantity from another specimen of the lichen, and completely purified. This substance is an acid, *leiphæmic acid*, $C_{22}H_{46}O_5$, crystallising in long needles melting at 114—115°. This lichen contains 2 per cent. of leiphæmic acid, about 0·8 per cent of atranoric acid, 1·5 per cent. of zeorin, and 1 per cent. of leiphæmin. Other specimens of this lichen, growing on granite, were found to contain the same substances in the same proportion. In distinction to *Hæmatomma coccineum*, no trace of usnic acid was found in this species.

New analyses of protolichesteric acid point to the formula $C_{19}H_{32}O_4$ or $C_{19}H_{34}O_4$; the earlier analyses (Abstr., 1902, i, 788) were incorrect, the percentage of carbon being too low. K. J. P. O.

*cyclo*Geraniolenealdehyde. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 141973 and 142139).—cyclo*Geraniolenealdehyde*, $CMe_2<\begin{smallmatrix}CH_2—CH\\CH_2\cdot CHMe\end{smallmatrix}>C\cdot CHO$ or $CMe_2<\begin{smallmatrix}CH{=}{=}CH\\CH_2\cdot CHMe\end{smallmatrix}>CH\cdot CHO$, is prepared by distilling calcium hydroxy*cyclo*geraniolanecarboxylate (this vol., i, 502) with calcium formate under reduced pressure as a colourless, fragrant oil, boiling at 101—102° under 17 mm. pressure.

C. H. D.

Derivatives and Condensation Products of β-Hydroxy-α-naphthaldehyde. ANDRÉ HELBRONNER (*Bull. Soc. chim.*, 1903, [iii], 29, 878—882).—*β-Acetoxy-α-naphthaldehyde*, prepared by acetylating the sodium derivative of the hydroxyaldehyde, is crystalline, melts at 87°, and is readily soluble; the *benzoyl* derivative, similarly prepared, crystallises in needles and melts at 109°.

When β-ethoxy-α-naphthaldehyde (1 mol.) is heated at 120° with ethyl cyanoacetate (1 mol.), the condensation *product*,

$$OEt\cdot C_{10}H_6\cdot CH{:}C(CN)\cdot CO_2Et,$$

is obtained. This forms lemon-yellow crystals, melts at 71°, and is readily soluble; sulphuric acid dissolves it forming a fluorescent solution, whilst prolonged ebullition with potassium hydroxide solution leads to the formation of malonic acid. The substance is not reduced by sodium amalgam.

The action of β-ethoxy-α-naphthaldehyde (1 mol.) on acetylacetone (1 mol.) in presence of sodium ethoxide yields *β-ethoxy-α-naphthylideneacetylacetone*, $OEt\cdot C_{10}H_6\cdot CH{:}CHAc$, which crystallises in orange-tinted needles and melts at 112°. The analogous *β-methoxy-α-naphthylideneacetylacetone* melts at 171°.

T. A. H.

Relations between Physical Properties and Molecular Weights of *p*- and *m*-Nitrosobenzaldehydes. FREDERICK J. ALWAY and WALTER D. BONNER (*Amer. Chem. J.*, 1903, 30, 111—115).—*p*-Nitrosobenzaldehyde forms yellow crystals, whilst the *m*-compound is white (compare Alway and Welsh, this vol., i, 263). Both aldehydes are green in the liquid state and in solution. Piloty has now shown (Abstr., 1902, i, 734) that white nitroso-compounds are bimolecular, the green colour being due to the unimolecular form. Both *p*- and *m*-nitrosobenzaldehyde show the normal molecular weight in boiling benzene and in freezing acetic acid solutions. In freezing benzene solution, the former is unimolecular, while the latter is partially associated, and its green colour becomes less intense as the freezing point is approached. The anomalous colour of *p*-nitrosobenzaldehyde is therefore unexplained.

C. H. D.

Additive Reactions with Nitrous Gases. HEINRICH WIELAND (*Annalen*, 1903, 328, 154—255).—After a *résumé* of our present knowledge of the constitution of the additive compounds formed from nitrous gases and compounds with doubly linked carbon atoms, the following conclusions are drawn: (1) aliphatic and hydroaromatic complexes form true nitrosites and nitrosates, thus:

$$[CMe_2(O\cdot NO)\cdot CHMe\cdot NO]_n,$$

and to this class belong the numerous derivatives of the terpenes. (2) Phenyl-substituted olefines yield the *pseudo*-nitrosites, thus:

$$\begin{array}{l} OMe\cdot C_6H_4\cdot C \text{——} CMe \\ \qquad\qquad\quad\; | \qquad\;\; | \\ \qquad\qquad\quad N\cdot O\cdot N \\ \qquad\qquad\quad\; | \qquad\;\; | \\ \qquad\qquad\quad O \text{——} O \end{array}.$$

(3) When a negative group is attached to the unsaturated side-chain, the capability of forming a *pseudo*-nitrosite decreases; ethyl phenyl*iso*crotonate forms a *pseudo*-nitrosite, but benzylideneacetophenone does not. In this case, three different reactions may occur: (i) a nitro-group becomes attached to the α-, and a nitroso-group to the β-carbon atom, forming a compound which then undergoes the following series of changes: $Ph\cdot CH(NO)\cdot CH(NO_2)\cdot CO\cdot R \longrightarrow$

$$Ph\cdot C(:NOH)\cdot C(NO_2):C(OH)\cdot R \longrightarrow \begin{array}{l} Ph\cdot C\cdot C(NO_2):C\cdot R \\ \quad\;\; \| \qquad\qquad\quad\; | \\ \quad\;\; N \text{————} O \end{array};$$

an *iso*oxazole is therefore finally produced.

(ii) A nitronitrite is formed, thus: $CHPh(O\cdot NO)\cdot CH(NO_2)\cdot R$.

(iii) Nitration in the side-chain takes place; at the same time, nitration of the benzene nucleus in the *para*-position to the side-chain commonly occurs.

I. *Action of Nitrous Fumes on Benzylideneacetophenone.*—When nitrous fumes are passed into a cooled solution of benzylideneacetophenone in benzene, a crystalline *compound* separates, which decomposes at 125—130°, and dissolves in aqueous alkalis to a yellow solution, from which it is reprecipitated by carbon dioxide; it is considered to have one or other of the following formulæ:

$$[C_6H_4(NO_2)\cdot C(:NOH)\cdot CH(NO_2)\cdot CPh(OH)]_2O_2$$

or $[COPh\cdot CH(NO_2)\cdot CH(C_6H_4\cdot NO_2)\cdot N(OH)]_2O_2$, and is formed in accordance with the equation $2C_{15}H_{12}O + N_6O_4 = C_{30}H_{24}O_{13}N_6$.

Reduction with tin and hydrochloric acid leads to the production of a diamino*iso*oxazole, which shows that all the different nitrogen atoms in the molecule of this complex *anhydride* ("the primary product") are directly linked with carbon; on oxidation with permanganate, a mixture of *p*-nitrobenzoic and benzoic acids is obtained. Although the compound dissolves unchanged in cold solutions of alkalis, it is decomposed on warming into benzoic acid, and the oxime of α-*p*-dinitroacetophenone, $NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CH_2\cdot NO_2$, a fact which demonstrates that nitrogen trioxide has become attached to the ethylene linking of the benzylideneacetophenone. When the ethereal solution of the anhydride is treated with dry ammonia, cleavage of the molecule takes place with the elimination of water, the benzoyl derivative of dinitroacetophenoneoxime, $NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CH(NO_2)\cdot COPh$, being formed. Of the two formulæ for the anhydride mentioned above, the former seems the most probable, as no phenylhydrazone is formed; the benzoyl derivative of dinitroacetophenoneoxime, on the other hand, yields a very unstable phenylhydrazone, which decomposes into benzoylphenylhydrazine and the oxime of α-*p*-dinitroacetophenone. The simplest compound having this peculiar type of linking would be the substance $OH\cdot CH_2\cdot O\cdot CH_2\cdot OH$, for which the name methyloloxide is suggested.

Under the influence of a variety of reagents, the complex anhydride is converted into a dinitro*iso*oxazole, $\begin{array}{l} CPh:C(NO_2)\cdot C\cdot C_6H_4\cdot NO_2 \\ | \qquad\qquad\quad\;\; \| \\ O \text{————} N \end{array}$; this substance is also readily formed from the benzoyl derivative of the

dinitro-oxime. The *iso*oxazole is stable towards most reagents, but is readily attacked by alcoholic potassium hydroxide, ethyl benzoate and α-p-dinitroacetophenoneoxime being formed. This oxime, unlike the mono-oximes of other 1 : 3-diketones, is only reconverted into the *iso*-oxazole by prolonged boiling with alcohol. On heating this dinitro-oxime or its benzoyl derivative with acids, α-p-dinitroacetophenone, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot NO_2$, is formed.

The diamino*iso*oxazole produced on reducing the complex anhydride with tin and hydrochloric acid is also obtained from the dinitro*iso*-oxazole.

In addition to the complex anhydride, which separates in crystals from the benzene solution on passing nitrous fumes, other substances are formed and remain as a yellow oil on evaporating the solvent. This oil contains β-p-dinitrobenzylideneacetophenone,

$$NO_2 \cdot C_6H_4 \cdot C(NO_2) \colon CHBz,$$

which, on hydrolysis, yields two series of hydrolytic products; on the one hand, nitrous and benzoic acids and p-nitrophenylacetylene, and on the other hand, p-nitrobenzoic and nitrous acids and acetophenone. On reduction, the dinitroacetophenone is converted into an amino*iso*-oxazole, $\begin{array}{l} NH_2 \cdot C_6H_4 \cdot C \cdot CH \colon CPh \\ \qquad\qquad\;\; N \text{——} O \end{array}$.

The major portion of the yellow oil consists of the *nitronitrite*, $CHPh(O \cdot NO) \cdot CH(NO_2) \cdot COPh$, an extremely unstable substance, which decomposes on keeping or on treatment with most reagents into benzoic and prussic acids, benzaldehyde, nitric oxide, and nitrous acid; it dissolves in alkali hydroxide with a yellowish-red coloration, and then decomposes in the manner just described; with alcohol, it reacts vigorously, ethyl nitrite being evolved, and a stable, crystalline compound, ethoxybenzylnitroacetophenone,

$$OEt \cdot CHPh \cdot CH(NO_2) \cdot COPh,$$

being formed; this substance readily yields benzaldehyde, ethyl alcohol, and α-nitroacetophenone. When the nitronitrite is treated with ethereal ammonia, benzaldehyde, nitrous acid, and the ammonium salt of α-nitroacetophenone are produced. These reactions all accord with the view that this compound is a nitronitrite; they might also be given by a dinitro-compound, $\cdot CH(NO_2) \cdot CH(NO_2) \cdot$, as this class of substances is known to be very unstable. Prolonged treatment of the ethereal solution of the nitronitrite with alkali effects the elimination of nitrous acid, benzylidene-α-nitroacetophenone,

$$CHPh \colon C(NO_2) \cdot COPh,$$

being formed, a change which leaves but little doubt as to the constitution of the original compound.

The p-4-*dinitro*-3 : 5-*diphenyl*iso*oxazole* mentioned is prepared by heating the complex anhydride (1 part) in solution in alcohol (6 parts); it crystallises in pale green leaflets melting at 199°, does not unite with bromine, and oxidises phenylhydrazine. p-4-*Diamino*-3 : 5-*diphenyl*iso-*oxazole* is obtained either by directly reducing the complex anhydride, or better by reducing the nitro*iso*oxazole with stannous chloride in alcoholic solution; the base crystallises with $\frac{1}{2}H_2O$ in yellow needles melting at 118° and decomposing at 195°; when oxidised with permanganate, prussic acid is formed, and with sodium nitrite and hydrochloric acid it yields a pale yellow diazo-compound. The *hydrochloride*

crystallises in pale yellow needles, which sinter at 170° and decompose at 200°; the *diacetyl* derivative is a well crystalline, stable compound melting at 250°.

p-α-*Dinitro-α-benzoylacetophenoneoxime* (p-ω-*dinitrodibenzoylmethaneoxime*), prepared in the manner previously described, from the complex anhydride, crystallises from benzene with ½ mol. of benzene in groups of very long needles, which sinter at 115° and melt and decompose at 131—132°; from acetic acid, it crystallises in yellow needles melting and decomposing at 136—137°. This compound yields a very unstable *potassium* derivative, and an unstable *acetyl* derivative, which is yellow and melts and decomposes at 158°. It reacts violently with phosphorus chloride, yielding benzoyl chloride and a substance which is free from chlorine. When boiled with alcoholic hydrochloric acid, it decomposes with ease into benzoic acid, hydroxylamine, and *α-p*-dinitroacetophenone. On reduction with tin and hydrochloric acid, a rose-coloured *hydrochloride* is formed, the base of which is soluble in water.

α-p-*Dinitroacetophenoneoxime*, which can be readily prepared from the complex anhydride, the dinitro*iso*oxazole, or from the corresponding benzoyl derivative by boiling with 5 per cent. alcoholic potassium hydroxide, crystallises in yellow needles melting and decomposing at 141°; the *potassium* derivative crystallises from alcohol in cinnabar-red needles. *α-p*-Dinitroacetophenone is prepared only with difficulty from its oxime or the benzoyl derivative of the latter, as it is so readily decomposed by acids into *p*-nitrobenzoic acid and nitromethane; it can best be obtained in a pure state by heating the oxime with 15 per cent. sulphuric acid for about half an hour; it melts at 148° (compare Thiele and Haeckel, this vol., i, 160).

β-p-*Dinitrobenzylideneacetophenone* is extracted by ether from the yellow oil obtained by passing nitrous fumes into the benzene solution of benzylideneacetophenone after filtering off the crystals of the complex anhydride and evaporating the solvent. The dinitro-compound separates in pale yellow leaflets, melting at 164° and decomposing at 170°; it forms about 3 per cent. of the oil, and in warm glacial acetic acid is oxidised by chromic acid to benzoic and *p*-nitrobenzoic acids. It is hydrolysed in the manner previously described; of the various products, p-*nitrophenylacetylene*, obtained by distilling the material in steam, crystallises in needles melting at 149° and has a sweet taste; it yields an explosive, yellow *silver* derivative and a brick-red *copper* derivative; on oxidation, *p*-nitrobenzoic acid is formed. p-*Aminodiphenyl*-iso*oxazole*, prepared by reducing the dinitro-ketone just mentioned, is isolated from the tin double salt and crystallises in needles melting at 155°; the *hydrochloride* becomes coloured at 235° and melts and decomposes at 259°; the *platinichloride* is a pale brown salt. This base has also been obtained by reducing *p*-nitrodiphenyl*iso*oxazole.

By evaporating the ethereal mother liquor, from which the dinitrobenzylideneacetophenone had separated, the above-mentioned *nitronitrite* can be isolated as an oil; it could not be further purified.

Benzylidene-α-nitroacetophenone is most conveniently prepared from the original yellow oil, which for this purpose is dissolved in ether and repeatedly shaken with ice-cold 2 per cent. aqueous sodium hydroxide; a small quantity of the sodium derivative of nitroacetophenone crystallises

out and the extraction with the alkaline solution is continued until nitrous acid is no longer found, whereon the ether is evaporated, leaving an oil which soon solidifies. The pure compound crystallises in thick plates melting at 90°, and is decomposed by aqueous alkalis and ammonia in ethereal solution into α-nitroacetophenone and benzaldehyde; under the influence of the former reagents, other decompositions occur simultaneously.

α-Nitroacetophenone is readily prepared from benzylideneacetophenone by evaporating the ethereal solution of the yellow oil, which has been extracted with aqueous sodium hydroxide, and adding an ethereal solution of ammonia, when the ammonium salt of the aceto phenone separates; the nitro-ketone melts at 106° and has the properties ascribed to it by Lucas (Abstr., 1899, i, 433).

α-Ethoxybenzylnitroacetophenone is prepared either by heating the yellow oil with a slight excess of ethyl alcohol until the evolution of ethyl nitrite and prussic acid has ceased, or by boiling benzylidenenitroacetophenone with alcohol; it crystallises in plates, melts at 119°, and decomposes at 185°, but boils at about 155° under 10 mm. pressure; it is quite insoluble in aqueous alkali, but is dissolved and decomposed by these reagents in alcoholic solution, yielding mainly benzaldehyde and *β-nitro-α-ethoxystyrene* (*α-phenyl-β-nitrovinyl ethyl ether*),

$$OEt\cdot CPh\colon CH\cdot NO_2,$$

which is a yellow oil completely volatile under reduced pressure (b. p. 143° under 14 mm. pressure), insoluble in aqueous, but soluble in alcoholic, alkalis.

II. *Action of Nitrous Fumes on Cinnamaldehyde.*—From the product of the action of nitrous fumes on cinnamaldehyde, two substances have been isolated in the pure state, phenylnitro*iso*oxazole,

$$CPh\leqslant\begin{matrix}C(NO_2)\colon CH \\ N\text{———}O\end{matrix},$$

and phenylnitroglyoxime peroxide, $\begin{matrix}CPh\colon N\text{——}O \\ C(NO_2)\colon N\cdot O\end{matrix}$; in addition, a *substance*, $C_8H_4O_4N_2$, has been obtained in yellow crystals melting at 143°; it is possibly *β-p*-dinitro-α-phenylacetylene; finally, an unstable yellow oil forms a considerable proportion of the products, this resembles very closely the oil obtained from benzylideneacetophenone, as it decomposes giving benzaldehyde, prussic acid, and ethyl nitrite when treated with alcohol.

*4-Nitro-3-phenyl*iso*oxazole* is prepared by saturating with nitrous fumes a solution of cinnamaldehyde in acetic acid and keeping the product for 24 hours; on pouring the solution into water, a mixture of crystals and oil separate. The crystalline *iso*oxazole is purified either by draining on porous tile or by washing with alcohol; it crystallises in yellow prisms melting at 116°, is oxidised by permanganate to benzoic acid, and oxidises both phenylhydrazine and hydroxylamine. It dissolves slowly in moderately concentrated aqueous sodium hydroxide, and separates again unchanged on acidifying. As the structure of the *iso*oxazole does not permit of direct salt formation, it is probable that the ring is broken in this process and that the salt is a derivative of the *α-nitro-β-oximinoenol*, $CPh(\colon NOH)\cdot C(NO_2)\colon CH\cdot OH$, which im-

mediately passes back into the *iso*oxazole when set free from its salts. On warming the aqueous solution of this sodium salt, benzonitrile, nitromethane (?), benzoic, prussic, and nitrous acids are formed.

The nitro*iso*oxazole dissolves in alcoholic alkali hydroxides forming a colourless solution, which contains a *salt* of an unstable *iso*oxazoline, produced by the addition of alcohol, $CPh\lessgtr\begin{matrix}C(:NO\cdot OH)\cdot CH(OEt)\\ N\text{———————}O\end{matrix}$; when this solution is warmed with excess of alkali hydroxide, a violent reaction takes place, the potassium salt of nitromethane, benzonitrile, and carbon dioxide being formed. If methyl alcohol is substituted for ethyl alcohol, benzonitrile and the *potassium* derivative of methyl nitroacetate, $NO_2K\colon CH\cdot CO_2Me$, are produced. This crystallises in yellow leaflets decomposing at 242°, and, on acidification, yields *methyl nitroacetate*, which is a colourless liquid boiling at 107° under 28 mm. pressure; it mixes with water and forms explosive salts. When the dry potassium salt is shaken with a chloroform solution of bromine, *methyl bromonitroacetate*, $NO_2\cdot CHBr\cdot CO_2Me$, is obtained; it is a colourless liquid boiling at 103° under 15 mm. pressure and quite insoluble in water; the *ammonium* salt forms colourless crystals melting and decomposing at 143°; the *silver* salt forms colourless crystals which, on heating, decompose, producing silver bromide. The potassium salt of methyl nitroacetate reacts with a solution of benzenediazonium chloride, giving the *phenylhydrazone*, $N_2HPh\colon C(NO_2)\cdot CO_2Me$, which crystallises in orange-yellow leaflets melting at 74° and decomposing at 110°, and forms a *potassium* derivative crystallising in thin, cinnabar-red, very explosive plates. On allowing methyl nitroacetate to remain dissolved in excess of alkali hydroxide, it is decomposed into methyl alcohol, potassium carbonate, and the potassium derivative of nitromethane; methyl bromonitroacetate undergoes a similar decomposition, bromonitromethane being formed.

4-*Amino-3-phenyl*iso*oxazole*, $CPh\lessgtr\begin{matrix}C(NH_2)\colon CH\\ N\text{———}O\end{matrix}$, is prepared by reducing the corresponding nitro-derivative with aluminium amalgam, and is a yellow oil boiling at 179° under 12 mm. pressure; it can be diazotised. The *acetyl* derivative crystallises in needles melting at 128—129°; the *hydrochloride* is a white powder; the *oxalate* is well crystalline, and the *platinichloride* forms yellowish-brown cubes.

The mother liquor remaining in the preparation of the potassium salt of methyl nitroacetate contains the *potassium* derivative of an acid, $\begin{matrix}CH\colon C(NO_2)\text{—}CO\\ C(NO_2K)\cdot CPh\colon N\end{matrix}\!\!>O$ (?), which is probably formed by the condensation of molecular proportions of 4-nitroso-3-phenyl*iso*oxazole and methyl nitroacetate with the elimination of methyl alcohol; this salt crystallises in orange-red needles, and the free acid in yellow plates which are very easily decomposed by acids.

Phenylnitroglyoxime peroxide is contained in the alcoholic extract of the primary product of the reaction of nitrous fumes with cinnamaldehyde, and is isolated by distilling with steam the residue left on evaporation. The solid distillate is dissolved in ether and thoroughly extracted with dilute sodium hydroxide to destroy the *iso*oxazole; the

peroxide crystallises in pale yellow leaflets melting at 100°, is soluble in water, and stable towards acids and oxidising agents. When reduced with stannous chloride and hydrochloric acid, it yields *phenylaminoglyoxime peroxide*, $\begin{array}{l}CPh:N——O\\ | \qquad\qquad\quad |\\ C(NH_2):N\cdot O\end{array}$, a non-basic substance crystallising in needles melting at 135—136°.

Phenylethoxyglyoxime peroxide, $\begin{array}{l}CPh:N——O\\ | \qquad\qquad\quad |\\ C(OEt):N\cdot O\end{array}$, is formed as a by-product in the isolation of 4-nitro-3-phenyl*iso*oxazole, and is found in the ethereal solution which has been shaken with alkali hydroxide; it is also obtained by adding alcoholic alkali hydroxide to an alcoholic solution of the peroxide; it separates in large crystals melting at 83°, and is volatile in steam. The corresponding *methoxy*-derivative is obtained in a similar manner, and forms rhombic plates melting at 69°.

Phenylhydroxyglyoxime peroxide, $\begin{array}{l}CPh:N——O\\ | \qquad\qquad\quad |\\ C(OH):N\cdot O\end{array}$, which has strong acid characters, is prepared by shaking an ethereal solution of the nitroperoxide with 8—10 per cent. aqueous sodium hydroxide, when the whole of the compound passes from the ether into the alkaline solution; it is obtained on acidifying as a microcrystalline powder, melting and decomposing at 133°.

The chemical changes described in this paper are discussed at considerable length, and are contrasted with many reactions of an analogous type. K. J. P. O.

Nitro-derivatives of α-Arylaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 142052).—When α-*p*-toluidinoanthraquinone is nitrated in suspension in glacial acetic acid and the product is warmed, a nitro-compound separates on cooling, which crystallises from pyridine in bright red needles, insoluble in water or aqueous alkalis. Similar compounds are obtained by nitration of α-anilinoanthraquinone, α-*m*-xylidinoanthraquinone, and α-naphthylaminoanthraquinone. C. H. D.

Distillation of Camphorimide with Soda-Lime; a Contribution to the Explanation of the peculiar Disruption of the Camphornitrilic Acids, on the Distillation of their Calcium Salts. JULIUS BREDT and K. WORNAST (*Annalen*, 1903, **328**, 338—348).—Tiemann, Lemme, and Kerschbaum (Abstr., 1901, i, 18) obtained, by the distillation of the calcium salts of both the α- and β-camphornitrilic acids, the same substance, αγ-dimethyl-Δ^{δ}-heptenonitrile, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CN$, the formation of which was thought to be due to the migration of a cyano-group. It is now shown that α-camphornitrilic acid is converted into camphorimide, which then yields β-camphornitrilic acid, from which alone can the heptenonitrile be directly produced.

Camphorimide can be prepared by saturating a solution of camphoric anhydride in alcohol with dry ammonia, evaporating the solvent, and distilling the residue; but it can be far more conveniently prepared

by slowly distilling camphoric acid in a stream of dry ammonia (an operation first carried out by Berzelius) and redistilling the product in order to free it from the anhydride. On distilling the imide with soda-lime, the heptenonitrile forms the main part of the distillate; it is an oil boiling at 89—90° under 14 mm. and at 202° (with slight decomposition) under the ordinary pressure. When the calcium salt of α- or β-camphornitrilic acid is distilled with soda-lime, the same nitrile is formed, but the first portion of the distillate contains some camphorimide. When hydrolysed with a methyl alcoholic solution of potassium hydroxide, the heptenonitrile is converted into the acid (b. p. 136—137° under 13 mm. pressure), also obtained from it by the above-mentioned authors. This acid is now shown to be identical with that obtained by Crossley and Perkin (Trans., 1898, 73, 8) by fusing camphoric acid with sodium hydroxide, both of them boiling under the ordinary pressure at 240—242°, and yielding on oxidation α-methylglutaric acid and acetone. K. J. P. O.

Gurjun Balsam. ALEXANDER TSCHIRCH and L. WEIL (*Arch. Pharm.*, 1903, 241, 372—400).—*Balsamum Dipterocarpi* (gurjun- or gardjan-balsam, garjantel, wood-oil) is a product of various species of the genus *Dipterocarpus*, indigenous in South Asia. About 80—82 per cent. of it consists of an *essential oil*, which can be removed by distillation with steam; this boils at 255° and has sp. gr. 0·912 at 15°. Of the residue, *gurjoresen*, $C_{17}H_{28}O_2$, forms the chief part, amounting to 16—18 per cent. of the balsam; it is amorphous and melts at 40—43°. Only about 3 per cent. of the balsam consists of resin *acids*; the bulk of these dissolves in 1 per cent. ammonium carbonate solution and is amorphous; the rest is insoluble, but dissolves in 1 per cent. sodium carbonate solution; this part was obtained to some extent in a crystalline state.

The deposits, largely crystalline in character, which had formed in various samples of gurjun balsam, were submitted to examination. They consist of crystalline resin-alcohols or resin-phenols, but yet are insoluble in alkalis, in these respects resembling amyrin, $C_{30}H_{50}O$. A substance obtained from Hirschsohn, and designated by him "neutral substance from gurjun balsam," consisted of such a hydroxy-compound, *gurjuresinol*, $C_{15}H_{25}\cdot OH$, probably identical with metacholestol (Mach, Abstr., 1895, i, 384) and copaivic acid (Keto, Abstr., 1902, i, 167); it melts at 131—132° and forms *acetyl* and *benzoyl* derivatives melting at 96° and 106—107° respectively. The crystalline *gurjuturboresinol*, from *Dipterocarpus turbinatus*, has the composition $C_{20}H_{30}O_2$, and melts at 126—129°; it is probably identical with Merck's copaivic acid and Trommsdorff's metacopaivic acid (Brix, Abstr., 1882, 65). A comparison of the properties of these substances is given in a table. Hirschsohn's "sodium salt from gurjun balsam," when purified by recrystallisation, contained 3·6 per cent. of sodium; it consists of gurjuresinol along with the sodium salt of *gurjoresinolic acid*, $C_{16}H_{26}O_4$; the acid is crystalline and melts at 254—255°. C. F. B.

Ericolin. A. KANGER (*Chem. Zeit.*, 1903, 27, 794—796).—Previous authors have given very varying analyses, ranging, for example, from

34 to 82 per cent. for carbon, of the glucoside "ericolin" present in the leaves of the cowberry (*Vaccinium vitis idaea*). This is probably due either to incomplete desiccation of the substance analysed, or to some decomposition occurring during its extraction by water or while drying. A product extracted from the leaves by ether-alcohol was purified from foreign substances by precipitating these in aqueous solution by means of lead acetate, the excess of the reagent being removed by hydrogen sulphide. The purified substance was completely soluble in ether-alcohol and had, approximately, the composition $C_{16}H_{25}O_{10}$. It is doubtful, however, whether this product is a definite chemical individual, as it is of a resinous nature, and there are no means of ascertaining its purity. W. A. D.

Examination of some Samples of Aloe from the Cape. J. Aschan (*Arch. Pharm.*, 1903, **241**, 340—357).—The product of *Aloe ferox* yielded *feroxaloin*, $C_{16}H_{18}O_7,H_2O$ or $C_{16}H_{16}O_7,H_2O$, when it was digested with water containing a few drops of hydrochloric acid, the filtered solution being treated with ammonia and calcium chloride; the precipitate produced was decomposed with a slight excess of hydrochloric acid and crystallised from water and then from alcohol; the aloin gave a negative result when examined by Zeisel's method. No aloin was obtained by a method which was successful in the case of other aloes from the Barbadoes and Natal: the aloe is dissolved in methyl alcohol, the extract mixed with chloroform and a little water and shaken, the chloroform layer run off, and the residual liquid extracted repeatedly with the same solvent. A little emodin, $C_{15}H_{10}O_5$, was obtained instead of aloin. The insoluble *resin* is different from that of other aloes examined hitherto; it is a glucoside, and is hydrolysed by dilute sulphuric acid to a sugar and *feroxaloresinotannol*, $C_{20}H_{18}O_6$, which yields chrysamic acid when oxidised with dilute nitric acid.

Another sample of unknown origin, unlike any of the usual types, proved to be Natal aloe when examined chemically.

Crystals which had separated from the fresh juice of aloes from Curacao were found to consist of emodin.

A tabular comparison of the reactions of various aloins is given.

C. F. B.

Constituents of Kô-Sam Seeds (Brucea Sumatrana). Frederick B. Power and Frederic H. Lees (*Pharm. J.*, 1903, [iv], **17**, 183—188).—The seeds of *Brucea sumatrana*, employed in the East Indies as a remedy for dysentery, have been asserted by Heckel and Schlagdenhauffen to contain quassin and a second bitter substance (*Rev. des Cult. Colon.*, 1900, 97). The seeds were subsequently examined by Bertrand (*ibid.*, 1900, 196), who stated that they contained a bitter, amorphous glucoside, kosamin, and 19·5 per cent. of oil. The authors find that these seeds contain a small quantity of formic acid and of volatile esters of butyric acid (?), 20 per cent. of an oil consisting of glycerides of oleic, linoleic, stearic, and palmitic acids, and in association with this the hydrocarbon, hentriacontane and a colourless, crystalline *substance*, $C_{20}H_{34}O$, which melts at 130—133°, has $[\alpha]_D$ $-37·7°$ in chloroform at 23°, and is probably allied to the cholesterols. There

are also present in the seeds two amorphous bitter *substances*, one of which is readily soluble in chloroform and sparingly so in ether, and the other insoluble in chloroform; both are soluble in water. Neither of these substances is identical with quassin nor is there any evidence that either is a glucoside. The seeds also contain 1·8 per cent. of tannic acid, a reducing sugar yielding an osazone which melts at 204—205°, and an enzyme capable of hydrolysing amygdalin, but no evidence of the presence of an alkaloid was obtained. T. A. H.

[Thermochemistry of] Cinchona Alkaloids. MARCELLIN P. E. BERTHELOT and GAUDECHON (*Ann. Chim. Phys.*, 1903, [vii], 29, 443—480).—See this vol., ii, 197, 270. C. H. D.

Opium Bases. OSWALD HESSE (*J. pr. Chem.*, 1903, [ii], 68, 190—207. Compare Goldschmiedt, Abstr., 1886, 83, 478; 1887, 163; 1888, 1116; 1889, 167).—Of five specimens of "papaverine" examined, four were found to contain papaverine and two to contain ψ-papaverine. Papaverine, $C_{20}H_{21}O_4N$, melts at 146—147°, is easily soluble in dilute alcohol or hot absolute alcohol, and dissolves in concentrated sulphuric acid to a colourless solution which becomes rose-coloured and purple-violet when strongly heated. The oxalate, $C_{20}H_{21}O_4N,C_2H_2O_4$, crystallises in slender needles or thick prisms and decomposes at 195°; the hydrochloride melts at 210—213° with evolution of methyl chloride and formation of protopapaverine; the hydriodide, $C_{20}H_{21}O_4N,HI$, crystallises in colourless, monoclinic, thick prisms which become yellow on exposure to air; it melts at 196°: the thiocyanate crystallises in colourless, slender needles or thick prisms and melts at 152°.

ψ-Papaverine, $C_{21}H_{21}O_4N$, is easily soluble in chloroform, more so than papaverine in absolute alcohol at 15°, and dissolves in concentrated sulphuric acid to a colourless solution. The hydrochloride,

$$C_{21}H_{21}O_4N,HCl,$$

forms thick, monoclinic crystals and melts and decomposes with formation of protopapaverine (?) at 208—210°; the *platinichloride*, $2C_{21}H_{21}O_4N,H_2PtCl_6$, is an orange-coloured, crystalline powder; the hydrogen oxalate crystallises in colourless needles and melts at 196°; the *thiocyanate* forms colourless, delicate needles and melts at 150°; the *hydriodide*, $C_{21}H_{21}O_4N,HI$, crystallises in thick, yellow prisms and melts and decomposes at 193°; from dilute alcohol, it crystallises in colourless prisms containing $3H_2O$.

Protopapaverine, $C_{19}H_{19}O_4N$, crystallises in yellow leaflets, decomposes at 260°, is only slightly soluble in alcohol, insoluble in ether, benzene, or chloroform, forms a dark brownish-red coloration with alcoholic ferric chloride, and dissolves in concentrated sulphuric acid to a colourless solution which becomes purple-violet on warming. The *hydrochloride*, $C_{19}H_{19}O_4N,HCl,5H_2O$, crystallises in yellow prisms and melts when anhydrous at 200°; the *platinichloride*,

$$2C_{19}H_{19}O_4N,H_2PtCl_6,5H_2O,$$

is a yellow, flocculent precipitate, which changes to an orange-coloured, crystalline powder; the *hydrobromide*, $C_{19}H_{19}O_4N,HBr,5H_2O$, forms octohedral crystals; the *hydriodide*, $C_{19}H_{19}O_4N,HI,3H_2O$, crystallises in brownish-yellow prisms; the *nitrate* is a yellow, granular, crystalline powder; the *oxalate*, $C_{19}H_{19}O_4N,C_2H_2O_4,5H_2O$, crystallises in yellow

octahedra or prismatic crystals, loses $5H_2O$ at 100°, and melts at 138°. With aqueous potassium hydroxide, protopapaverine forms a potassium compound which, when acted on by methyl iodide, forms protopapaverine and protopapaverine methiodide (Pictet and Kramers, Abstr., 1903, i, 358).

Papaveramine, $C_{21}H_{25}O_6N$, obtained as a soluble oxalate in the purification of papaverine, crystallises in thin, colourless prisms, melts at 128—129°, is easily soluble in chloroform, almost insoluble in water, and forms an intensely bluish-violet solution in concentrated sulphuric acid. The *hydrochloride* crystallises in stellate groups of prisms; the *platinichloride*, $2C_{21}H_{25}O_6N,H_2PtCl_6,3H_2O$, forms a light yellow, flocculent precipitate. G. Y.

Double Haloids of Tellurium with the Alkaloids. VICTOR LENHER and WINIFRED TITUS (*J. Amer. Chem. Soc.*, 1903, **25**, 730—732).—When a strong solution of tellurium dioxide in hydrochloric or hydrobromic acid is added to a strong solution of an alkaloid in the corresponding acid, a thick, curdy precipitate of the double haloid is formed, the final purification being effected by crystallisation from hot dilute acid solution. These double haloids are stable at the ordinary temperature; they are decomposed by water with precipitation of tellurous acid and are readily dissolved by dilute acids.

Quinine tellurichloride, $C_{20}H_{24}O_2N_2,2HCl,TeCl_4$, begins to decompose at 150° and is decomposed by water at the ordinary temperature. The corresponding *cinchonine* salt, $C_{19}H_{22}ON_2,2HCl,TeCl_4$, forms light yellow crystals; the *strychnine* salt, $(C_{21}H_{22}O_2N_2,HCl)_2,TeCl_4$, separates in large, bright yellow needles; the *morphine* salt, $(C_{17}H_{19}O_3N,HCl)_2,TeCl_4$, forms dark yellow crystals and is the most stable of the series towards heat; the *theobromine* salt, $(C_7H_8O_2N_4,HCl)_2,TeCl_4$, and the *brucine* salt, $(C_{23}H_{26}O_4N_2,HCl)_2,TeCl_4$, are yellow.

Quinine telluribromide forms bright red crystals easily decomposable by heat. The *cocaine*, *brucine*, and *morphine telluribromides* separate in red crystals. A. McK.

Compounds of Metallic Haloids with Organic Bases. CARL RENZ (*Zeit. anorg. Chem.*, 1903, **36**, 100—118. Compare Abstr., 1902, i, 393, 563).—The following double compounds of metal haloids and organic bases have been prepared:

Indium chloride pyridine, $InCl_3,3C_5H_5N$, slender, white needles, not hygroscopic, soluble in alcohol, but insoluble in ether. *Indium chloride pyridine hydrochloride*, $InCl_3,3(C_5H_5N,HCl)$, small crystals, insoluble in ether. *Indium chloride quinoline hydrochloride*,

$$InCl_3,4(C_9H_7N,HCl),$$

white needles, insoluble in ether, soluble in hydrochloric acid or alcohol. *Niobium chloride piperidine*, $NbCl_5,6C_5H_{11}N$, white, hygroscopic needles. *Niobium iodide pyridine hydriodide*,

$$NbI_5,6(C_5H_5N,HI),$$

long, brown needles, soluble in alcohol, insoluble in ether. No compound of niobium chloride with aniline, dimethylaniline, or quinoline could be obtained. *Ruthenium chloride quinoline hydrochloride*, $RuCl_3,2(C_9H_7N,HCl)$, brown needles, insoluble in ether and in acetone. *Iridium chloride pyridine*, $IrCl_4,2C_5H_5N$, light brown,

crystalline powder soluble in water to a yellow solution. *Iridium chloride quinoline*, $IrCl_4,C_9H_7N$, reddish-brown, crystalline powder. *Glucinum chloride quinoline*, $GlCl_2,2C_9H_7N,H_2O$, yellow, hygroscopic needles, soluble in alcohol but insoluble in ether. *Thallium chloride diquinoline*, $TlCl_3,2C_9H_7N$, crystallises from alcohol in white plates with a silvery lustre which melt at 183°. It has not been possible to obtain again the triquinoline compound previously described (*loc. cit.*). *Thallium iodide quinoline*, $TlCl_3,C_9H_7N$, red crystals. *Gold chloride pyridine*, $AuCl_3,C_5H_5N$, lemon-yellow, crystal powder which melts at 225°. *Gold chloride quinoline*, $AuCl_3,C_9H_7N$, yellow crystals. *Uranium tetrachloride quinoline*, UCl_4,C_9H_7N, small, yellow crystals.

A table is given of all the double compounds of metal haloids with pyridine and quinoline which have been described. J. McC.

Acetylation of some Amino-derivatives of the Naphthalene and Quinoline Groups. S. Cybulsky (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 219—223).—The author has measured the limit of acetylation, and the velocity after half an hour, for a mixture of 1 mol. of acetic acid and one of an amine when heated in a sealed tube at 210°; the results are as follows:

Amine.	Velocity after half an hour.	Limit
Aniline	68·71	73·54 per cent.
α-Naphthylamine	35·5	47·49 ,,
β-Naphthylamine	69·1	82·8 ,,
α-Tetrahydronaphthylamine	63·3	decomposes
β-Tetrahydronaphthylamine	89·7	95·3 per cent.
Tetrahydroquinoline	16·80	35·42 ,,
8-Methyltetrahydroquinoline	1·24	23·70 ,,
7-Methyltetrahydroquinoline	12·52	29·67 ,,
6-Methyltetrahydroquinoline	20·73	40·02 ,,

Comparing the results obtained for aniline with those of Menschutkin (Abstr., 1882, 1084), it is seen that as the temperature rises the acetylation limit diminishes.

The relative magnitudes of the above numbers correspond with those obtained by Menschutkin (Abstr., 1902, ii, 493) for the combination of these compounds with alkyl bromides, and confirm this author's conclusions regarding the influence of the side-chain on reactivity.

T. H. P.

3-Benzyl*iso*quinoline. Leopold Rügheimer (*Annalen*, 1903, **328**, 326—337. Compare this vol., i, 438).—3-Benzyl*iso*quinoline is formed together with the 4-isomeride when benzoyltetrahydro*iso*quinoline is heated with benzaldehyde (*loc. cit.*), and has now been obtained in larger quantity by an improvement in the method of separation; the oily residue left after the removal of 4-benzyl*iso*quinoline is dissolved

in ether and extracted with 40 per cent. sulphuric acid; from the latter solvent, a mixture of sparingly soluble sulphates slowly crystallises; from a hot aqueous solution of this mixture, the sulphate of the 3-isomeride separates first. This base crystallises from alcohol in prisms, which belong to the triclinic system, melts at 104°, and boils at 311° under 23 mm. pressure. The *hydrochloride* crystallises in needles, the *sulphate* and *nitrate* separate in needles, the latter melting at 136—137°; the *platinichloride* crystallises with H_2O in small needles, which, when anhydrous, melt at 216—217°; the *mercurichloride*, $(C_{16}H_{13}N)_7,(HCl,HgCl_2)_5$, crystallises in flattened needles, becomes coloured at 205°, and melts and decomposes at 213—214°. The *picrate* forms aggregates of needles melting at 199°.

The paper also includes a description of a simple form of pressure regulator for distillations under reduced pressure. K. J. P. O.

Phenolic Urethanes of Piperidine. Bouchetal de la Roche (*Bull. Soc. chim.*, 1903, [iii], 29, 752—756. Compare Abstr., 1902, i, 562, and this vol., i, 574).—The following substituted *urethanes* were prepared by the interaction of piperidine with phenyl carbonates: 2 : 4 : 6-*trichlorophenylpiperidylurethane*, $C_6H_2Cl_3\cdot O\cdot CO\cdot C_5NH_{10}$, from 2 : 4 : 6-trichlorophenol, forms colourless crystals, melts at 75°, and boils at 227° under 25 mm. pressure; the corresponding compound from *o*-bromophenol melts at 63°; the isomeric substance from *p*-bromophenol melts at 66—67° and boils at 245° under 52 mm. pressure; the urethane from 2 : 4 : 6-tribromophenol melts at 60—61°, and boils at 218° under 40 mm. pressure. o-*Nitrophenylpiperidylurethane*,

$$NO_2\cdot C_6H_4\cdot O\cdot CO\cdot C_5NH_{10},$$

from *o*-nitrophenol, melts at 77°, and boils at 226—227° under 21 mm. pressure; the isomeride from *p*-nitrophenol melts at 94—95° and boils at 272° under 52 mm. pressure; 3-*bromo*-p-*tolylpiperidylurethane*, from 3-bromo-*p*-cresol, melts at 75—76° and distils at 262° under 34 mm. pressure.

When the urethane prepared from phenol and piperidine is boiled with a solution of bromine in chloroform, only a small proportion of brominated urethane is formed, most of the product consisting of tribromophenol and piperidine hydrobromide. The urethanes are easily hydrolysed by warm concentrated aqueous alkali hydroxides, giving the phenol, carbon dioxide, and piperidine, whilst the alcoholic hydroxides bring about the same decomposition at the ordinary temperature. Aromatic bases, for example, aniline and toluidine, interact with the urethanes only in sealed tubes at 250°, giving not mixed carbamides, but the constituents of the original urethane. Concentrated sulphuric acid decomposes the urethanes, giving a sulphonated phenol, and nitric acid fails to give definite products. Tin and hydrochloric acid do not act on the phenolic urethanes of piperidine except those containing a nitro-group; in such cases, an aminophenol is formed. W. A. D.

Yellow Dyes of the Acridine Series. Badische Anilin- & Soda-Fabrik (D.R.-P. 141356).—Phthalyl derivatives of *m*-diamines are heated with the hydrochloride of the diamine at 220°, with or without addition of zinc chloride, or the diamine hydrochloride is

heated directly with phthalic anhydride. The product from phthalyl-*m*-tolylenediamine has the composition of a *diaminodimethylphenylacridinecarboxylic acid*, and dissolves in water or alcohol to a yellow solution with a moss-green fluorescence. C. H. D.

Azo-dyes of the Santonin Series. Oskar Schmidt and Edgar Wedekind (*Zeit. Farb. Text.-Chem.*, 1903, 2, 229—233).—A brief account of the chemistry of santonin is first given.

Desmotroposantoninazosulphanilic acid, $C_{21}H_{24}O_7N_2S$, prepared from detmotroposantonin, $CO<\begin{matrix}O\text{———}CH\cdot CH_2\cdot C\cdot CMe\colon CH\\ CHMe\cdot CH\cdot CH_2\cdot C\cdot CMe\colon C\cdot OH\end{matrix}$, and diazosulphanilic acid, crystallises from alcohol in glistening, red leaflets melting at 269°. Its aqueous solution in sodium carbonate is reddish-yellow, whilst its solutions in sodium and potassium hydroxides are dark violet. The *aniline* derivative crystallises in yellow needles, the p-*toluidine* derivative forms bright red crystals. o-*Nitrobenzeneazodesmotroposantonin* crystallises from benzene in brilliant dark red needles. The dye, prepared from o-*tolidine* and desmotroposantonin, is soluble with difficulty even in alkalis; it softens at about 285° and melts at 290°. The nitroazo-dye from *p*-nitroaniline and *d*-santoninic acid crystallises from alcohol in bright red leaflets melting at 175°, and is soluble with difficulty in alkalis. The dye, formed from diazobenzenedisulphonic acid and *d*-santoninic acid, dissolves in sodium hydroxide solution to a dark red liquid. Diaminostilbenedisulphonic acid and desmotroposantonin yield a brownish-red dye soluble in sodium carbonate solution. A similar compound was prepared from diaminostilbenedisulphonic and *d*-santoninic acid.

Since the santonin derivatives used in the preparation of these dyes are derivatives of tetrahydronaphthol, they behave like phenols and not like naphthols. A. McK.

Hydrazidines. Hugo Voswinckel (*Ber.*, 1903, 36, 2483—2487).—Whilst phenylhydrazine acts on acetoiminoethyl ether to form diphenylethenylhydrazidine, with other iminoethers examined, the products were not hydrazidines of the type of diphenylethenylhydrazidine, but a mixture of formazyl derivatives of the type $NHPh\cdot N\colon CR\cdot N\colon NPh$, and hydrazidines of the type $NHPh\cdot N\colon CR\cdot NH_2$.

Diphenylethenylhydrazidine hydrochloride,

$$NHPh\cdot N\colon CMe\cdot NH\cdot NHPh\cdot HCl,$$

prepared by the action of phenylhydrazine on acetoiminoethyl ether hydrochloride or by the reduction of methylformazyl by ammonium sulphide, forms glistening leaflets, which melt and decompose at 142°. The free base is unstable, since, when liberated from the hydrochloride, it is instantly transformed into methylformazyl.

Benzenylphenylhydrazidine hydrochloride, $NHPh\cdot N\colon CPh\cdot NH_2,HCl$, prepared from phenylhydrazine and benziminoethyl ether hydrochloride, crystallises in transparent prisms and melts at 132°; it contains $\frac{1}{2}H_2O$ and becomes anhydrous at 110°. The *free* base is a colourless oil, which gradually darkens owing to decomposition.

Benzenylcarbanilphenylhydrazidine, $NHPh\cdot N\colon CPh\cdot NH\cdot CO\cdot NHPh$,

prepared from benzenylphenylhydrazidine hydrochloride by adding excess of sodium carbonate solution and then phenylcarbimide, forms stellate prisms, which melt and decompose at 168°.

Phenylethenylphenylhydrazidine hydrochloride,

$$CH_2Ph\cdot C(:N\cdot NHPh)NH_2,HCl,$$

prepared from phenylacetoiminoethyl ether and phenylhydrazine, crystallises in transparent prisms, and melts and decomposes at 226°; benzylformazyl is produced as a by-product. The free base crystallises from a mixture of benzene and light petroleum in transparent plates melting and decomposing at 70°.

Benzylformazyl, $CH_2Ph\cdot C(:N\cdot NHPh)N:NPh$, forms a brilliant red, amorphous powder melting at 127°. On reduction with ammonium sulphide, it yields *phenylethenyldiphenylhydrazidine*,

$$CH_2Ph\cdot C(:N\cdot NHPh)NH\cdot NHPh,$$

which forms transparent, stellate prisms; from this, benzylformazyl is readily regenerated by heating, or, more slowly, by the action of light. A. McK.

Action of Phenylhydrazine on Alkyl Bromides and Iodides. J. Allain Le Canu (*Compt. rend.*, 1903, **137**, 329—331).—The author has extended the work on this subject commenced by Genvresse and Bourcet (Abstr., 1899, i, 501). By the action of an alkyl haloid on phenylhydrazine, it has been possible to isolate salts containing one, two, and three molecules of phenylhydrazine, and compounds with one molecule of phenylhydrazine and two alkyl groups.

When phenylhydrazine is added to a concentrated solution of ethyl bromide in alcohol, *dibasic phenylhydrazine hydrobromide*,

$$(N_2H_3Ph)_2HBr,$$

is formed, but is quickly transformed into the monobasic salt, and at the same time a neutral compound, $N_2H_2Et_2PhBr$, is produced, and can be separated on account of its great solubility in alcohol. Precisely the same reaction takes place with methyl or ethyl iodide. The crystals of $N_2H_2Me_2PhI$, although large, have dull, striated faces, whilst those of $N_2H_2Et_2PhI$ are brilliant; like the corresponding diethylbromo-compound, these crystals are orthorhombic. *n*-Propyl iodide reacts similarly; in very concentrated solution, a *tribasic phenylhydrazine hydriodide*, $(N_2H_3Ph)_3,HI$, is formed, and changes rapidly into the dibasic, then into the monobasic, salt. By extraction with ether, it is possible to obtain the neutral compound, $N_2H_2Pr^{a}{}_2PhI$, which crystallises in monoclinic needles. With *iso*amyl iodide, the reaction is much slower, but ultimately ammonium iodide is formed; if the action be carried out carefully, it is possible to isolate tribasic and dibasic phenylhydrazine hydriodide. On shaking vigorously, a crystalline powder, $N_2H_2(C_5H_{11})_2PhI$, is formed. The crystals are monoclinic and slightly coloured; they are easily soluble in alcohol, but only sparingly so in cold water. J. McC.

Preparation of a Blue Sulphur Dye. Clayton Aniline Co., Ltd. (D.R.-P. 140964).—A solution of the sodium salts of dimethyl-*p*-

phenylenediamine and dihydroxyphenyl disulphide,

$$C_6H_4{<}{\substack{S\text{———}S \\ ONa\ \ HO}}{>}C_6H_4$$

(Haitinger, Abstr., 1883, 988), when oxidised with sodium hypochlorite, gives rise to a blue *compound*, which probably has the following constitution: $NMe_2{\cdot}C_6H_3{\overset{N}{\diagup\!\!\diagdown}}C_6H_2{<}{\substack{S\text{—}S \\ O\ \ O}}{>}C_6H_2{\overset{N}{\diagup\!\!\diagdown}}C_6H_4{\cdot}NMe_2$. This product, when salted out, is a blue powder with coppery lustre; it dissolves in cold sodium sulphide solution with a blue colour which disappears on heating. C. H. D.

Formation of Carbamide by the Oxidation of Albumin with Permanganate EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1903, 39, 210—211).—Polemical. A reply to Jolles (this vol., i, 723). J. J. S.

Hydrolysis of Casein and Silk-fibroin by Acids. EMIL FISCHER (*Zeit. physiol. Chem.*, 1903, 39, 155—158. Compare Abstr., 1901, i, 780, 783; 1902, i, 654).—Serine and pyrrolidine-α-carboxylic acid have been obtained from the hydrolytic products of casein, and a small amount of pyrrolidine-α-carboxylic acid among those from silk-fibroin. J. J. S.

Glucothionic Acid from Tendon Mucin. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1903, 39, 1—3).—Glucothionic acid gives on distillation a marked furfuraldehyde reaction. Its reactions point to the presence of glycuronic acid in its molecule, but the hydrazone from *p*-bromophenylhydrazine could not be prepared. E. F. A.

Nucleohiston of the Thymus. WILLEM HUISKAMP (*Zeit. physiol. Chem.*, 1903, 39, 55—72).—Nucleohiston from thymus can be separated by precipitation with 0·7 per cent. sodium chloride into α- and β-forms containing 4·5 and 3·05 per cent. of phosphorus respectively. Both yield on extraction with dilute hydrochloric acid the same nuclein containing 7·5 per cent. of phosphorus.

The behaviour of nucleohiston towards acids shows it to contain weak basic groups, and the salts it forms with acids are all highly dissociated. E. F. A.

Preparation and Analysis of Nucleic Acids. IV. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1903, 39, 4—8. Compare this vol., ii, 438).—Pancreas nucleic acid, on hydrolysis with 25 per cent. sulphuric acid under pressure at 175°, forms amongst other products uracil and the two pyrimidine bases, thymine and cytosine, the first of these three substances being obtained in small quantities only. Yeast nucleic acid contains no thymine, but relatively large quantities of uracil and cytosine. E. F. A.

Preparation and Analysis of Nucleic Acids. V. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1903, 39, 133—135. Compare this vol., i, 668; ii, 438).—The nucleic acid of liver has been obtained by a method

similar to that employed for other nucleic acids, but it has been found difficult to free it from biuret. This is best accomplished by suspending the copper salt in water, adding hydrochloric acid insufficient for complete decomposition, dissolving the acid salt in a solution of sodium hydroxide and Rochelle salt and carefully precipitating the acid with hydrochloric acid. When hydrolysed with 25 per cent. sulphuric acid at 150—175°, the nucleic acid yields both thymine and cytosine together with traces of uracil. J. J. S.

Optical Activity of the Nucleic Acid of the Thymus Gland. ARTHUR GAMGEE and WALTER JONES (*Proc. Roy. Soc.*, 1903, **72**, 100—103).—Nucleic acid was prepared from the thymus by the Kossel-Neumann method. It forms perfectly transparent solutions. The value of $[\alpha]_D$ varied between $+154·2°$ and $+156·9°$; it does not vary appreciably with dilution. On acidification of the solution with acetic acid, $[\alpha]_D$ rises gradually as the acidity increases to $+164·7°$, and with more acid then decreases. Ammonia decreases and finally abolishes the optical activity, but neutralisation by acid restores it to its former value. W. D. H.

Action of Trypsin. MORITZ SCHWARZSCHILD (*Beitr. chem. Physiol. Path.*, 1903, **4**, 155—170).—As in previous researches by Gulewitsch and by Gonnermann, a number of simple substances were subjected to the action of trypsin. Some belonged to the group of the acid amides, others were substances which give the biuret reaction. The substances investigated, and in which a negative result was obtained, were asparagine, acetamide, urea, benzamide, oxamide, biuret, octaspartic acid, malonodiamide, glycinamide, ethyloxamide, amino-oxalazide, phenyloxamide, hippuric acid, and piperazine. The only positive result was in the case of Curtius's base (ethyl hexaglycylglycinate); this gives an intense biuret reaction, which in 4—6 days completely disappears under the action of trypsin. Hofmeister has already pointed out the similarity of this substance to proteids, and the type of union, $·NH·CH_2·CO·NH·$, appears to be that which trypsin can unlock: the absence of an asymmetric carbon atom in Curtius's base is of interest. W. D. H.

Preparation of Guanylic Acid. IVAR BANG and C. A. RAASCHOU (*Beitr. chem. Physiol. Path.*, 1903, **4**, 175—181).—Guanylic acid, a nucleic acid obtainable from the pancreas, is a substance of considerable interest, as it contains only one purine base, namely, guanine, and also yields the pentose (*l*-xylose), which has been separated from that gland. Hitherto, the method of preparation has been difficult, and the present paper describes a simplified method, which has enabled the authors to prepare 100 grams of pure material. At one stage in the operations, a guanylic acid is obtained which differs from that previously described by containing one more glycerol-pentose group. This is termed α-guanylic acid; it is convertible into the other β-variety by boiling with alkali. The α-acid contains 6·65, and the β-acid 7·64 per cent. of phosphorus. W. D. H.

Influence of Carbohydrates on Proteid Putrefaction. S. Simnitzki (*Zeit. physiol. Chem.*, 1903, 39, 99—125).—The decomposition of sugar and proteid in a putrefying mixture begins at the same time, but does not progress equally rapidly. The presence of sugar inhibits the decomposition of proteid by bacteria, and the amount of decomposed proteid is nearly in inverse proportion to the amount of sugar. The action of lactose in this direction is greater than that of dextrose, and that of dextrose more intense than that of galactose. This depends on the ease with which acids, and especially lactic acid, are formed from the different sugars. The effect is not felt in the later stages of putrefaction, when the appearance of ammonia takes place and the acid is neutralised. W. D. H.

Tryptophan, the Precursor of Indole in Proteid Putrefaction. Alexander Ellinger and Max Gentzen (*Beitr. chem. Physiol. Path.*, 1903, 4, 171—174).—Tryptophan is one, if not the only, precursor of the indole formed from proteids by bacterial decomposition.
W. D. H.

Precipitation of Proteids by Alcohol and other Reagents. M. Christine Tebb (*J. Physiol.*, 1903, 30, 25—38).—Egg globulin, like serum globulin, is composed of at least two proteids, one insoluble in water (euglobulin), and the other soluble (pseudo-globulin). The true globulins (euglobulins) require considerably less alcohol to precipitate them than do the albumins. Although the pseudo-globulins are more readily salted out from solution than are the albumins, and less readily than the euglobulins, the precipitability by alcohol does not run quite parallel with this. On the whole, the pseudo-globulins resemble the albumins in their precipitability by alcohol; but in one case, that of egg-white, the albumin is more readily precipitable by alcohol than the pseudo-globulin. In the case of milk, lactalbumin is precipitable by alcohol with difficulty, and caseinogen, in spite of some resemblances between it and globulins, also requires a considerable amount of alcohol to precipitate it all; the greater portion, however, is thrown out of solution by a comparatively small amount of alcohol. Paramyosinogen appears to be the euglobulin of muscle, whereas myosinogen, the pseudo-globulin, requires more alcohol to precipitate it. These statements are supported by analytical figures. From the analogy of the colloid and crystalline carbohydrates, the view is taken that the true globulins have larger molecules than the pseudo-globulins and albumins; this is supported by the facts of disease; the damaged kidney cells in Bright's disease are least permeable to the euglobulin of the blood. The prolonged action of alcohol renders euglobulins readily insoluble; the pseudo-globulins and caseinogen come next, whilst albumins are much more difficult to convert into insoluble modifications by the use of this reagent. Proteids of still smaller molecular size, such as proteoses and peptones, require not only a large amount of alcohol to precipitate them, but also are not rendered insoluble by prolonged contact with alcohol.

Purified egg albumin is precipitable by ether; serum albumin and lactalbumin are not. Egg pseudo-globulin is precipitable by ether, so

also are both globulins of serum, but there are differences of detail; serum pseudo-globulin, for instance, is most readily precipitable by ether when in a neutral solution, and serum euglobulin when the solution is rendered acid. The precipitation, often in a jelly-like form, which occurs on the addition of ether to acidified serum, is due to the action of that reagent on the globulins.

The statements that (i) serum albumin is less readily precipitable by hydrochloric acid than egg albumin, and (ii) the coagulum produced by boiling egg albumin is soluble with difficulty in nitric acid, whereas that produced by boiling serum albumin is readily soluble in nitric acid, depend on experiments performed with unpurified products. On repeating them with solutions of the crystallised albumins, they were, however, found to be correct. W. D. H.

Proteid Matter in Maize Grains. E. Donard and Henri Labbé (*Compt. rend.*, 1903, **137**, 264—266. Compare this vol., ii, 215).—By extraction of maize with alcoholic potassium hydroxide, 9·84 per cent. of proteid matter was obtained. Extraction of this residue with amyl alcohol showed that 5·27 per cent. of the maize consisted of a soluble modification. Extraction with 90 per cent. ethyl alcohol showed that 6·90 per cent. of the maize was soluble in this. The proteid matter of maize therefore consists of three distinct proteids: *a-maisin*, soluble in amyl alcohol; *β-maisin*, insoluble in amyl alcohol, but soluble in 90 per cent. ethyl alcohol; and *γ-maisin*, insoluble in amyl and ethyl alcohols.

β-Maisin can be obtained by direct extraction of the maize grains with 90 per cent. alcohol, and has the composition: C = 55·50 per cent.; H = 7·85; O = 20·73; N = 14·58; S = 0·62; ash = 0·72, and is analogous in properties to α-maisin. It is assumed that the differences in constitution of the three maisins is very slight, perhaps only differing degrees of hydration. J. McC.

Peptones. Max Siegfried (*Zeit. physiol. Chem.*, 1903, **38**, 259—264).—The six following peptones, obtained by the aid of enzymes, have been isolated by the iron method (Abstr., 1902, i, 654). Trypsin-fibrinpeptone-α or antipeptone-α, $C_{10}H_{17}O_5N_3$; trypsin-fibrinpeptone-β or antipeptone-β, $C_{11}H_{19}O_5N_3$; pepsin-fibrinpeptone-α, $C_{21}H_{34}O_9N_6$; pepsin-fibrinpeptone-β, $C_{21}H_{36}O_{10}N_6$; pepsin-glutinpeptone, $C_{23}H_{39}O_{10}N_7$, and trypsin-glutinpeptone, $C_{19}H_{30}O_9N_6$. The formulæ given are the empirical formulæ calculated from the analytical data. All peptones are decided acids. They redden litmus and are capable of decomposing metallic carbonates; assuming the above formulæ, they are all monobasic acids. The homogeneity of the different preparations is emphasised by the fact that the composition does not vary after repeated precipitation, and that the rotatory power is also unaffected. It has been found that when the two antipeptones are precipitated repeatedly from aqueous solutions, their rotatory power gradually increases, but is immediately depressed to the original value when precipitated from water containing a small amount of acetic acid. By the action of trypsin on albumin, part is readily decomposed yielding amino-acids and bases; peptones are also formed; these do not contain

the tyrosine group and are extremely resistant to the further action of trypsin.

All six peptones on hydrolysis yield considerable amounts of glutamic acid. It is probable that the iron reaction characteristic of certain peptones is due to the presence of a glutamic or aspartic acid radicle in the molecule. J. J. S.

Antipeptones. FRITZ MÜLLER (*Zeit. physiol. Chem.*, 1903, 38, 265—285. Compare Siegfried, Abstr., 1901, i, 57; 1902, i, 654, and following abstract).—The antipeptone obtained by the tryptic fermentation of Kühne and Chittenden's antialbumid (Abstr., 1884, 849) is not a pure substance. Both antipeptones, α- and β-, may be obtained by the action of trypsin on fibrin, and may be readily isolated by Siegfried's iron process. Analyses agree with the empirical formulæ previously suggested by Siegfried: antipeptone-β from fibrin has $[\alpha]_D$ $-32·4°$ at 20°, and antipeptone-α from the same source, $[\alpha]_D$ $-24·61°$ at 20°. The rotation of the β-compound may be increased to $-40·9°$ after three precipitations from aqueous solutions, but at once assumes the normal value on precipitation from a solution containing a trace of acetic acid. When hydrolysed with 9 times its weight of 33·3 per cent. sulphuric acid, antipeptone-α yields arginine, which may be isolated in the form of its silver nitrate derivative, lysine, glutamic acid (12 per cent.), and aspartic acid.

Antipeptone-β also yields arginine on hydrolysis with sulphuric acid.

Antipeptone-β yields 16·1 and antipeptone-α 22 per cent. of its nitrogen in the form of ammonia on hydrolysis with sulphuric acid (33·3 per cent.). J. J. S.

Pepsin-fibrinpeptone. CURT BORKEL (*Zeit. physiol. Chem.*, 1903, 38, 289—319. Compare Mühle, *Diss. Leipzig*, 1901).—Fibrin is suspended in 0·5 per cent. hydrochloric acid and digested with pepsin for 3 weeks at 30—40° in the presence of chloroform and thymol. Albumoses are precipitated by the addition of aluminium sulphate and concentrated sulphuric acid, pepsinpeptone-α by addition of iron alum in neutral, and pepsinpeptone-β by iron alum in faintly acid, solution.

The following are the more important data:

Pepsinpeptone-α, $C_{21}H_{34}O_9N_6$, is a monobasic acid, and usually contains small amounts (0·73 per cent.) of sulphur. The molecular weight determined by the cryoscopic method in aqueous solution is 655. It has $[\alpha]_D$ $-36·36°$ at 20°, but this is increased by the presence of ammonia.

Pepsinpeptone-β, $C_{21}H_{36}O_{10}N_6$, contains no sulphur, has a mol. rot. about 532, and $[\alpha]_D$ ranging from $-20·17°$ to 26·85°; this is considerably increased by the presence of ammonia. When heated at 100°, the β-compound appears to be transformed by the loss of a molecule of water into the α-compound. The following products are obtained from the α-pepsinpeptone by the action of trypsin, namely, tyrosine, antipeptone-α and -β, arginine, but no lysine or histidine. These results indicate the presence of two "anti-" groups in pepsinpeptone.

J. J. S.

Epinephrine and its Compounds. Epinephrine Hydrate (Adrenaline). JOHN J. ABEL (*Amer. J. Pharm.*, 1903, **75**, 301—325. Compare Abstr., 1899, i, 395; 1900, i, 72; and this vol., i, 670).—An historical summary of previous investigations of the hæmostatic constituent of suprarenal gland secretion is given. It is shown that the suprarenine of von Furth (Abstr., 1899, ii, 115; 1900, ii, 292), the adrenaline of Takamine (Abstr., 1902, ii, 217. Compare Aldrich, *ibid.*, 518), and the "non-alkaloidal form" of epinephrine described by the author (*loc. cit.*) are all more or less pure forms of the substance $C_{10}H_{13}O_3N,\frac{1}{2}H_2O$, which it is now proposed to name epinephrine hydrate, the name epinephrine being reserved for the isomeric, anhydrous, physiologically inactive "alkaloidal form" obtained by the action of acids or alkalis on this hydrate. It is now admitted that epinephrine hydrate reduces Fehling's solution (compare Aldrich, *loc. cit.*). Nitric acid oxidises epinephrine and its hydrate to oxalic acid and a base having an odour resembling that of coniine or piperidine (compare Abstr., 1900, i, 72). T. A. H.

Preparation and Constitution of Histidine. ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1903, **39**, 212).—Polemical (compare Fränkel, this vol., i, 650). J. J. S.

Constitution of Histidine. FRITZ WEIGERT (*Zeit. physiol. Chem.*, 1903, **39**, 213).—Fränkel's formulæ for histidine (this vol., i, 651) are objected to, as neither contains an "asymmetric carbon atom," and histidine is an optically active substance. J. J. S.

Lactase. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1903, **137**, 56—59).—The authors have already suggested that the supposed decomposition of lactose by emulsin is in reality due to the lactase which frequently accompanies emulsin. In support of this view, it has been established that when almonds have been mascerated with water saturated with toluene, the filtrate is able to effect the decomposition of lactose. The decomposition was followed both polarimetrically and by formation of the osazones of the dextrose and galactose produced.

In various *Rosaceæ*, lactase occurs along with emulsin; in *Aspergillus niger* and *Polyporus sulfureus*, there is only emulsin, and in kephir there is lactase but no emulsin. J. McC.

Organic Chemistry.

Nature of Double Linkings. EMIL KNOEVENAGEL (*Ber.*, 1903, 36, 2803—2816).—In order to explain a number of abnormal properties shown by substances containing more than one double linking, it is assumed that the doubly-linked carbon atoms are in a state of oscillatory or continuous rotation. Thus, in the case of butadiene, the scheme proposed may be represented by the formulæ:

$$\mathrm{{}_{H}{>}CH{-}CH{=}CH{-}C{<}_{H}}$$
$$\mathrm{H{-}CH{=}CH{-}CH{=}C{-}H}\ ,$$
$$\mathrm{{}^{H}{>}CH{-}CH{=}CH{-}C{<}^{H}}$$

in which the *oscillatory* motion of the atoms results in the production, alternately with the compound containing two double linkings, of an isomeride containing one double linking and two terminal free bonds; the arrows indicate the direction of rotation required to reproduce the two double linkings from the alternative scheme of linkings; this theory explains the production from butadiene of the dibromide, $\mathrm{Br{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}Br}$. In the case of benzene, alternate atoms are regarded as revolving *continuously* in opposite directions, the result being that the three double linkings travel continuously round the molecule.

Such a theory indicates the possibility of new types of isomerism which may be even more refined than optical isomerism, and it is suggested that many cases of supposed polymorphism, such as that of benzophenone and the quinols, are in reality manifestations of structural differences of this type, the author inclining towards Lehmann's view that differences of crystalline form afford *a priori* evidence of differences of molecular structure.

It is also suggested that the motion of the atoms renders the groups adjacent to a double linking especially active, and in this way the dissociation of hydrogen from benzyl alcohol, benzhydrol, and other compounds is accounted for. T. M. L.

Influence of Traces of Water on the Decomposition of Alkali Hydrides by Acetylene. HENRI MOISSAN (*Compt. rend.*, 1903, **137**, 463—466. Compare this vol., i, 595, and ii, 365).—Acetylene, prepared from calcium carbide and dried by contact with fused potassium hydroxide, has no action on the hydrides of the alkali metals at temperatures between $-80°$ and $+42°$ and under reduced pressure. At 42°, action takes place with incandescence. In presence of minute quantities of water, reaction occurs in the neighbourhood of $-60°$, commencing at one point in the hydride and extending rapidly throughout the whole mass. It was found that passage of the dried gas through caoutchouc tubing rendered it sufficiently "wet" to react

with the hydride (compare this vol., ii, 365). In one experiment, in which 3 mg. of ice were contained in a sealed tube together with potassium hydride and acetylene cooled to $-80°$, a portion of the hydride came into contact with the ice, producing a small quantity of potassium hydroxide. The vapour tension of the latter was sufficient to cause the formation of a minute layer of potassium acetylide over the hydride, but as the temperature did not rise to 42° at any point general decomposition did not ensue. T. A. H.

Constitution of the so-called Primary Dinitrohydrocarbons, $R\cdot CHO_4N_2$. GIACOMO PONZIO (*Gazzetta*, 1903, **33**, i, 412—416. Compare Abstr., 1901, i, 685, and 1902, i, 334; also Scholl, Abstr., 1902, i, 753).—The action of water on the potassium derivatives of the so-called primary dinitrohydrocarbons, $R\cdot CHO_4N_2$, yields ammonia, potassium nitrite, and the potassium salt of the acid $R\cdot CO_2H$. From this result and those already obtained (*loc. cit.*), the author concludes that these dinitro-compounds contain: (1) only one nitro-group capable of being determined by titration with standard stannous chloride; (2) only one atom of nitrogen directly united with a carbon atom, as is shown by the formation of primary amines on reduction; (3) an atom of oxygen combined directly with carbon, as is shown by the formation of aldehydes on heating and of acids by the action of mineral acids; (4) an oximic group, $:N(OH)$, from which is derived the ammonia formed by the action of water. These compounds are hence to be regarded as nitrohydroxamic acids having the constitution

$$OH\cdot N:CHR\cdot O\cdot NO_2.$$

When heated with water in a sealed tube, potassium dinitropropane yields ammonia, and potassium nitrite and propionate. Potassium dinitrobutane and potassium dinitrononane behave similarly.

T. H. P.

Fermentation Amyl Alcohol. ANTON KAILAN (*Monatsh.*, 1903, **24**, 533—567).—Bemont (Abstr., 1902, i, 131) concluded that fermentation fusel oil consists mainly of *d*-β-methylbutyl alcohol, and imagined that he had isolated the pure optically active constituent of fusel oil when he obtained a fraction boiling at 131—131·5°. The author shows that Bemont's conclusions are incorrect (compare Marckwald and McKenzie, Abstr., 1901, i, 248; Marckwald, Abstr., 1902, i, 418).

Fermentation amyl alcohol from various sources was oxidised by chromic acid and the resulting valeric acids were converted into their silver salts, solubility determinations of which were then made. Since the solubility in water of silver β-methylbutyrate is very much less than that either of the *r*-α-methylbutyrate, or of the *d*-(or *l*-)-α-methylbutyrate, the values actually obtained showed that most of the specimens of fermentation amyl alcohol examined consisted mainly of the inactive *iso*amyl alcohol (γ-methylbutyl alcohol). The values for the specific rotation of the alcohol obtained from molasses show that this alcohol contained about 50 per cent. of the active constituent (compare Marckwald, *loc. cit.*), but the silver salt of the acid, prepared by oxidation of the alcohol, consisted mainly of silver β-methylbutyrate. A. McK.

Methyl and Ethyl Ethers of Acetylcarbinol and some of their Derivatives. GIOVANNI LEONARDI and M. DE FRANCHIS (*Gazzetta*, 1903, 33, i, 316—322).—The ethyl ether of acetylcarbinol can be readily detected when in small quantity by the action of *p*-nitrophenylhydrazine in alcoholic solution, which yields the p-*nitrobenzylhydrazone*, $OEt\cdot CH_2\cdot CMe:N\cdot NH\cdot C_6H_4\cdot NO_2$, crystallising from a mixture of light petroleum and benzene in silky, yellow needles melting at 101—102°.

By converting methyl propargyl ether into the compound

$$2C_4H_6O,3HgCl_2,3HgO$$

and boiling this with excess of 5 per cent. hydrochloric acid, the *methyl ether* of *acetylcarbinol*, $CH_2Ac\cdot OMe$, is obtained as a colourless liquid having a fruity acid odour and boiling at 112—114°; it is miscible in all proportions with water and reduces Fehling's solution and ammoniacal silver nitrate in the cold. Its *phenylhydrazone*, $C_{10}H_{14}ON_2$, which forms an amber-yellow oil boiling and slightly decomposing at 186° under 24 mm. pressure, is soluble in ether or benzene.

Methoxymethylindole, $C_{10}H_{11}ON$, obtained (together with another *substance* which separates from a mixture of light petroleum and benzene in pale yellow crystals melting at 137—138°, and is probably an osazone of the methyl ether of acetylcarbinol) by condensing the above phenylhydrazone in presence of excess of phenylhydrazine, crystallises from water in colourless, shining needles melting at 82—83°; it has a characteristic fœcal odour and is soluble in alcohol or ether.

The methyl ether of acetylcarbinol can also be characterised by means of its p-*nitrophenylhydrazone*, which crystallises from a mixture of light petroleum and benzene in silky, lemon-yellow crystals melting at 110—111°.

The action of semicarbazide on the methyl or ethyl derivative of acetylcarbinol does not yield a semicarbazide, but a decomposition product of this, namely, hydrazodicarbonamide,

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$$

(Abstr., 1892, 1298). T. H. P.

The Glycol from *iso*Valeraldehyde and *iso*Butaldehyde. VIKTOR JELOČNIK (*Monatsh.*, 1903, 24, 526—532).—Löwy and Winterstein (Abstr., 1901, i, 626), by the action of 30 per cent. sulphuric acid on the glycol from *iso*valeraldehyde and *iso*butaldehyde, obtained an unsaturated hydrocarbon, C_9H_{16}, an oxide, $C_9H_{18}O$, an oxide $C_{18}H_{36}O_2$, and a fourth substance boiling at 175°. The author has repeated Löwy and Winterstein's experiments and has studied not only the action of sulphuric acid in varying dilutions, but also the action of water alone on the glycol. The hydrocarbon and the two oxides of Löwy and Winterstein were obtained, and it is concluded that the fourth substance prepared by these investigators was a mixture of the two oxides. A. McK.

Action of Dilute Sulphuric Acid on the Glycol from *iso*Valeraldehyde. MAX MORGENSTERN (*Monatsh.*, 1903, 24, 579—589).—*iso*Valeraldehyde, prepared by oxidation of commercial amyl alcohol, was condensed with alkali to form the glycol, $C_{10}H_{22}O_2$ (compare

Rosinger, Abstr., 1901, i, 669), which crystallises from dilute alcohol in needles and melts at 48°. It is optically inactive. It was heated with twice its weight of 12 per cent. sulphuric acid for 10 hours at 150—160°; the resulting oil was then separated from the aqueous layer and, when dried, was fractionated under the ordinary pressure. The small fraction boiling at 108—112° was possibly an aldehyde of the composition $C_{10}H_{20}O$. The fraction boiling at 138° contained the unsaturated hydrocarbon, $C_{10}H_{18}$, a clear mobile liquid of a turpentine-like odour, insoluble in water and volatile with steam; it forms an additive compound with bromine. The fraction boiling at 171° is an oxide, $C_{10}H_{20}O$, a yellow liquid of a turpentine-like odour; it is neither ketonic nor aldehydic in nature. The substance boiling at 169° under 16 mm. pressure is also an oxide, $C_{20}H_{40}O_2$, a yellow, viscid liquid; when it is heated at 100° in a sealed tube with hydrobromic acid and then boiled with potassium carbonate solution, the glycol, $C_{10}H_{22}O_2$, is regenerated. A. McK.

Nitroso-organic Anhydrides. Luigi Francesconi and U. Cialdea (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 74—75).—Mixed anhydrides of nitrous acid and an organic acid can, in general, be prepared by the action of nitrosyl chloride on the silver salt of the organic acid.

Nitrosoacetic anhydride, NO·OAc, obtained in this way, is a golden-yellow liquid which decomposes rapidly in direct sunlight and more slowly in diffused light, and when heated yields a violently explosive vapour. T. H. P.

Natural and Synthetical Mixed Glycerides of Fatty Acids. Hans Kreis and August Hafner (*Ber.*, 1903, 36, 2766—2773).—*β-Palmityldistearin* is prepared by heating αγ-distearin with palmitic acid (compare this vol., i, 457), and crystallises from ether or light petroleum in microscopic needles melting at 63°. After fusion, the mass has a double melting point, at 52·2° and 62° (compare Abstr., 1902, i, 529). The glyceride obtained from lard melts at 51·8° and 66°, and is not identical with α- or β-palmityldistearin. An examination of the fatty acids proved that no palmitic acid was present, but an acid having the formula $C_{17}H_{34}O_2$, melting at 55—56° and probably identical with daturic acid. Guth (this vol., i, 225) was unable to prepare mixed glycerides containing oleic acid; this may be effected, however, by distilling distearin or dipalmitin with oleic acid under reduced pressure. The yield is small, and a certain quantity of tristearin or tripalmitin is always formed at the same time; it is therefore impossible to indicate the position of the acid groups in the molecule.

Oleodistearin crystallises from ether-alcohol in microscopic needles melting at 42°, and, after fusion, at 28—30° and 42°. The naturally occurring oleodistearin, isolated from cocoa butter and mkani-fat, melts at 27—28° and 44—45° and is probably an isomeride.

C. H. D.

Action of Magnesium and Carbon Dioxide on Allyl Bromide. A New Synthesis of Vinylacetic Acid. JOSEPH HOUBEN (*Ber.*, 1903, 36, 2897—2900).—Vinylacetic acid,

$$CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H,$$

has been prepared by Wislicenus (Abstr., 1899, i, 736) from sodium β-bromoglutarate, and by Fichter and Krafft (Abstr., 1899, i, 255) by distilling β-hydroxyglutaric acid. It is found that Grignard's method for the synthesis of carboxylic acids may be applied in this case. Magnesium ribbon is covered with absolute ether, and a current of carbon dioxide is passed through, allyl bromide being gradually added. A vigorous reaction takes place, and the flask must be cooled from time to time in water. When the gas is no longer absorbed, the mass is poured on to ice and extracted with ether to remove unaltered allyl bromide. The residual liquid is then acidified and extracted with ether, and the acid purified by distillation. The calcium salt crystallises from hot or cold water with $1H_2O$. Fichter and Krafft's salt with $2H_2O$ could not be prepared. C. H. D.

Oxidation of Oleic Acid by Potassium Permanganate in Presence of Small Quantities of Alkali. DAVID HOLDE and J. MARCUSSON (*Ber.*, 1903, 36, 2657—2662).—On oxidising oleic acid by potassium permanganate in presence of just sufficient alkali hydroxide to neutralise the acid, not only is dihydroxystearic acid formed, but also a considerable quantity of a *hydroxyketostearic acid*,

$$CH_3{\cdot}[CH_2]_7{\cdot}CO{\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CO_2H$$

or $CH_3{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H$; this crystallises from light petroleum or 60 per cent. alcohol, melts at 63—64°, and gives an oily *acetyl* derivative, which, from an analysis of its *silver* salt, has the composition $C_{18}H_{33}O_3{\cdot}OAc$. The keto-acid gives a *phenylhydrazone* melting at 102·5—105°, and a *semicarbazone*, $C_{19}H_{37}O_4N_3$, melting at 134—135°, and, on oxidation with cold chromic acid in acetic acid solution, is converted into the corresponding θι-diketo-acid, $C_{18}H_{32}O_4$, which melts at 83—84° and is identical with stearoxylic acid. That the foregoing keto-acid is not formed by the oxidation of dihydroxystearic acid initially produced is shown by the fact that this acid, under the conditions used, is hardly attacked by permanganate, and yields only 5 per cent. of the diketo-acid. Hazura has suggested that oleic acid is transformed into dihydroxystearic acid by the hydrolysis of a glycide-like compound, $\begin{matrix} CH_3{\cdot}[CH_2]_7{\cdot}CH \\ CO_2H{\cdot}[CH_2]_7{\cdot}CH \end{matrix}\!\!>\!O$, by the alkali arising from the potassium permanganate, but this view appears doubtful since ammonium permanganate gives rise to the same products as the potassium salt, and a direct addition of two hydroxyl groups seems more probable. W. A. D.

Action of Nitrogen Peroxide on Unsaturated Acids of the Series $C_nH_{2n-2}O_2$. I. IWAN W. EGOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 358—375. Compare Demjanoff, Abstr., 1899, i, 845).—On mixing a light petroleum solution of acrylic acid with liquid nitrogen peroxide, the solution being meanwhile kept cool, crystals gradually

separate, which are found to consist of a mixture of the mononitro-compound, $C_3H_4O_2(NO_2)\cdot OH$, and the dinitro-compound, $C_3H_4O_2(NO_2)_2$. The syrupy residue obtained after separation of the crystals also contains these two substances.

When nitrogen peroxide is passed through a carefully cooled alcoholic solution of methyl acrylate, a yellow product is obtained which consists of a mixture of the mononitro-, $C_4H_6O_2(NO_2)\cdot OH$, and dinitro-derivatives, $C_4H_6O_2(NO_2)_2$. On heating this product with hydrochloric acid in a sealed tube, it yields methyl chloride, hydroxylamine, and oxalic acid. When the mixed nitro-compounds are reduced by means of tin and hydrochloric acid, a crystalline product is obtained, which melts at 234—235° and is identical with *iso*serine (β-amino-α-hydroxypropionic acid) (compare Fischer and Leuchs, Abstr., 1902, i, 268, and this vol., i, 12); with phenylcarbimide, it gives a carbamide derivative of the constitution $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CH(OH)\cdot CO_2H$, which melts at 178—180°. T. H. P.

Action of Nitrogen Peroxide on Acids of the Series $C_nH_{2n-2}O_2$. II. Action of Nitrogen Peroxide on Crotonic and *iso*Crotonic Acids and on Ethyl Crotonate. Iwan W. Egoroff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 466—482. Compare preceding abstract).—If crotonic acid or its ethyl ester is treated in ethereal solution at a low temperature with nitrogen peroxide, the products of the reaction undergo profound decomposition during the removal of the ether, so that what is obtained in either case is a mixture of dinitro- and nitro-oxidation products.

Using light petroleum as solvent, the same product, namely, *α-nitro-β-hydroxybutyric acid*, $OH\cdot CHMe\cdot CH(NO_2)\cdot CO_2H$, is obtained either from crotonic acid or from *iso*crotonic acid; it separates in crystals which melt at 119—121° and are soluble in alcohol, ether, chloroform, or ethyl acetate; it has the normal molecular weight in freezing acetic acid and yields an *acetyl* derivative soluble in acetic acid. Reduction of the acid with tin and hydrochloric acid yields *α-amino-β-hydroxybutyric acid*, $OH\cdot CHMe\cdot CH(NH_2)\cdot CO_2H$, which crystallises with $\frac{1}{2}H_2O$ and melts and decomposes at 229—230°; the *ammonium* salt melts and decomposes at 246° and the *hydrochloride* melts at 147—150°. Reduction of the aminohydroxy-acid by means of hydriodic acid and red phosphorus yields α-aminobutyric acid. T. H. P.

Action of Nitrogen Peroxide on Acids of the Series $C_nH_{2n-2}O_2$. III. Action of Nitrogen Peroxide on Methylacrylic Acid. Iwan W. Egoroff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 482—488. Compare preceding abstracts).—On treating a light petroleum solution of methylacrylic acid with nitrogen peroxide dissolved in the same solvent, the liquid being kept well cooled, a mixture of dinitro- and nitro-oxidation products is obtained which, when reduced with tin and hydrochloric acid, yields *β-amino-α-hydroxy-α-methylpropionic acid*, $NH_2\cdot CH_2\cdot CMe(OH)\cdot CO_2H$, which begins to turn yellow at 253° and melts and decomposes at 276°; it

has the normal molecular weight in boiling water; its *hydrochloride* melts at 132—134° and the *platinichloride* separates from water in plates or prisms melting and decomposing at 199—200°. Reduction of the acid by means of hydriodic acid and red phosphorus gave an uncrystallisable mass. The acid gives a hydroxamic acid when treated with Caro's persulphuric acid (compare Bamberger, Abstr., 1903, i, 324). T. H. P.

Preparation of Methyl Diethylacetoacetate. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1903, [iii], **30**, 954—955).—The author has applied the method described by Peters (Abstr., 1890, 1096) to the preparation of this ester. Metallic sodium (11·5 grams) was dissolved in methyl alcohol (70 grams) and the solution treated with the calculated quantities of ethyl iodide and ethyl acetoacetate, the mixture being warmed for two hours in a reflux apparatus. The mixture of methyl and ethyl ethylacetoacetates so produced was separated into its constituents by fractional distillation and these treated with ethyl iodide and sodium methoxide dissolved in methyl alcohol. In each case, the product was methyl diethylacetoacetate, the total yield being about 70 per cent. T. A. H.

Synthesis of α-Nitro-esters. C. ULPIANI (*Atti Real. Accad. Lincei*, 1903, [v], **12**, i, 439—443).—Compounds of the aliphatic series do not admit of direct nitration so readily as aromatic compounds, but an exception to this rule is met with in the case of ethyl malonate, which is acted on by fuming nitric acid, giving an almost theoretical yield of ethyl α-nitromalonate; the latter is a very stable substance and forms crystalline metallic derivatives more stable than the corresponding derivatives of ethyl malonate itself, and it lends itself to the preparation of aliphatic nitro-esters, of which but few are known. Thus, with methyl iodide, the ammonium derivative of ethyl α-nitromalonate yields ethyl nitro*iso*succinate:

$$MeI + NH_4\cdot C(NO_2)(CO_2Et)_2 = NH_4I + NO_2\cdot CMe(CO_2Et)_2,$$

and this, with sodium ethoxide, gives the sodium derivative of ethyl α-nitropropionate, from which ethyl α-nitropropionate may be obtained.

The *ammonium* derivative of *ethyl α-nitromalonate*,

$$NH_4\cdot C(NO_2)(CO_2Et)_2,$$

crystallises from water in yellow, hexagonal or rhombic plates, or from alcohol in white, rectangular plates melting and decomposing at 150°.

Ethyl nitro*iso*succinate was not obtained quite pure, but was converted into *ethyl sodio-α-nitropropionate*, $ONa\cdot CMe(NO)\cdot CO_2Et$, which crystallises from alcohol in slender, silky needles melting at 200°, and when treated with dilute hydrochloric acid gives *ethyl α-nitropropionate*, $OH\cdot CMe(NO)\cdot CO_2Et$, obtained as a thin, colourless oil boiling at 190—195° under the ordinary pressure and at 174° under 390 mm. T. H. P.

Synthesis of Cystin. EMIL ERLENMEYER, jun. (*Ber.*, 1903, **36**, 2720—2722).—The synthesis of *r*-serin has been effected by Erlenmeyer (this vol., i, 29) by condensing ethyl formate with ethyl hip-

purate to form ethyl formylhippurate, which, when reduced, gives ethyl monobenzoylserin, from which serin may be obtained by the action of dilute sulphuric acid. The synthesis of *r*-cystin has now been accomplished as follows. Ethyl monobenzoylserin is heated with phosphorous pentasulphide for 6 hours at 120°, when hydrogen sulphide is evolved; the product is then boiled for 8 hours with concentrated hydrochloric acid, the benzoic acid is filtered off, and the filtrate saturated with ammonia. The resulting cystein was not separated, but was directly converted into cystin by passing a current of air for three hours through the ammoniacal liquid. The product was acidified by glacial acetic acid, when *r*-cystin separated. The synthesis is represented thus: $HCO_2Et + NHBz{\cdot}CH_2{\cdot}CO_2Et \rightarrow CHO{\cdot}CH(NHBz){\cdot}CO_2Et \rightarrow OH{\cdot}CH_2{\cdot}CH(NHBz){\cdot}CO_2Et \rightarrow SH{\cdot}CH_2{\cdot}CH(NHBz){\cdot}CO_2Et \rightarrow SH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \rightarrow$

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H.$$

A. McK.

Cystin. A. J. Patten (*Zeit. physiol. Chem.*, 1903, 39, 350—355).—The fact that cystin is an important decomposition product of proteid matter is confirmed. Mörner states that cystin, and not cystein, is the primary product; this is so, but in the method of preparation adopted some of the cystin is transformed into cystein. For the identification of cystin, a well-defined crystalline product, cystinephenylhydantoin, is obtained by the action of phenylcarbimide.

W. D. H.

Triketones. III. Franz Sachs and Wilhelm Wolff (*Ber.*, 1903, 36, 3221—3235. Compare Abstr., 1901, i, 670; 1902, i, 837).—Although the alkali salts of triketones cannot be prepared, barium and lead derivatives are obtained by direct interaction with the metallic carbonates; these derivatives are, however, of different types. The *barium* derivative of $\beta\gamma\delta$-triketopentane,

$$OH{\cdot}CAc_2{\cdot}OBaO{\cdot}CAc_2{\cdot}OBaO{\cdot}CAc_2{\cdot}OH,$$

is a yellow, amorphous powder, which decomposes when heated and resembles the parent ketone in its reducing properties; the *lead* derivative, $CAc_2{<}{}^{O}_{O}{>}Pb,H_2O$, is white and sparingly soluble in water. The *barium* derivative of $\beta\gamma\delta$-triketo-δ-phenylbutane, $C_{30}H_{26}O_{12}Ba_2$, resembles that of triketopentane.

Triketones fail to give additive compounds with hydrogen chloride and hydrogen cyanide, but interact readily with acetylacetone, ethyl malonate, or *p*-nitrobenzyl cyanide. The *compound*, $OH{\cdot}CAc_2{\cdot}CHAc_2$, prepared by heating $\beta\gamma\delta$-triketopentane with acetylacetone at 100°, crystallises from benzene in colourless, rhombic leaflets and melts at 112°; the absence of two contiguous carbonyl groups in this compound may be inferred from its failing to interact with *o*-phenylenediamine in the cold, but no direct proof of the presence of hydroxyl can be obtained by means either of acetic anhydride or phenylcarbimide. The *compound*, $COPh{\cdot}CAc(OH){\cdot}CHAc_2$, obtained from acetylacetone and $\beta\gamma\delta$-triketo-δ-phenylbutane, crystallises from dilute acetic acid and melts at 103°. The *compound*, $OH{\cdot}CAc_2{\cdot}CH(CO_2Et)_2$, prepared from $\beta\gamma\delta$-triketopentane and ethyl malonate in presence of piperidine,

crystallises in rectangular leaflets and melts at 53°; the *substance*, $OH\cdot CAc_2\cdot CH(CN)\cdot C_6H_4\cdot NO_2$, obtained from the same compound and *p*-nitrobenzyl cyanide crystallises from a mixture of benzene and acetone in white leaflets and melts at 161—162°.

Piperidine added to well-cooled $\beta\gamma\delta$-triketopentane causes it to polymerise to a *compound*, $C_{10}H_{10}O_5$, which crystallises from benzene, melts at 119°, boils at 168° under 20 mm. pressure, and has no reducing properties; it gives a *phenylhydrazone*, $C_{10}H_{10}O_4\colon N_2HPh$, which crystallises from glacial acetic acid in lustrous, rhombic leaflets and melts at 249°; the analogous *semicarbazone*, $C_{10}H_{10}O_4\colon N_2H\cdot CO\cdot NH_2$, crystallises from the same solvent in leaflets and melts and decomposes at 256°.

The *polymeride*, $C_{20}H_{16}O_6$, prepared by the action of piperidine on $\beta\gamma\delta$-triketo-δ-phenylbutane dissolved in benzene, crystallises from glacial acetic acid and gives a *phenylhydrazone*, $C_{20}H_{16}O_5\colon N_2HPh$, which forms yellow crystals and melts at 241°; the analogous *semicarbazone* melts and decomposes at 265°. Together with the polymeride is formed a *substance*, $C_{20}H_{14}O_5$, which is more soluble in alcohol, and crystallises from it in yellow leaflets melting at 168°; the *phenylhydrazone*, $C_{20}H_{14}O_4\colon N_2HPh$, melts at 232°, and the *semicarbazone*, $C_{20}H_{14}O_4\colon N_2H\cdot CO\cdot NH_2$, at 239°.

[With Willy Kraft.]—*Preparation of $\alpha\beta$-Diketonic Esters.*

α-p-*Dimethylaminoanil* of *ethyl $\alpha\beta$-diketobutyrate*,

$$CO_2Et\cdot CAc\colon N\cdot C_6H_4\cdot NMe_2,$$

prepared by heating *p*-nitrosodimethylaniline dissolved in alcohol containing sodium carbonate with ethyl acetoacetate for $1\frac{1}{2}$ hours at 45°, crystallises from light petroleum in brownish-red, four-sided prisms and melts at 63·5°; when heated with dilute sulphuric acid, it gives a *compound*, $C_4H_6O_3$ (? ethyl glyoxalate, $CHO\cdot CO_2Et$), which crystallises in prisms and melts at 88°.

α-p-*Dimethylaminoanil* of *ethyl α-benzoyl-α-ketoacetate*,

$$CO_2Et\cdot CBz\colon N\cdot C_6H_4\cdot NMe_2,$$

prepared from ethyl benzoylacetate and *p*-nitrosodimethylaniline, crystallises in four-sided prisms and melts at 91·5°. W. A. D.

Hemi-celluloses. II. Ernst Schulze and Nicola Castoro (*Zeit. physiol. Chem.*, 1903, 39, 318—328).—The sugars obtained by dissolving the products of the hydrolysis of hemi-celluloses in alcohol consist of xylose, and also probably lævulose. In addition to this, there are products which dissolve in alcohol with difficulty; from these, an osazone was prepared melting at 205°, which is probably glucosazone. Hemi-cellulose therefore contains xylan, dextran, and lævulan groups, but not galactan or mannan groups, because no galactose or mannose was formed. The formation of starch from dextran and lævulan in the plant organism is easy to understand; the formation of starch from a pentosan is not so easy to explain, but nevertheless undoubtedly occurs. W. D. H.

Vegetable Mucilages. Albert Hilger (*Ber.*, 1903, 36, 3197—3203).—The mucilage of linseed may be isolated by extracting the seed with cold water and precipitating by pouring into alcohol.

After removal of mineral constituents by dilute hydrochloric acid and washing with alcohol and ether, the mucilage is obtained in a form which is completely soluble in water to an acid, dextrorotatory solution. Analysis shows pentosans and galactans to be present in molecular proportion, the formula being $C_6H_{10}O_5,C_5H_8O_4$. Hydrolysis with 0·5—1 per cent. sulphuric acid forms dextrose, galactose, arabinose, and xylose.

Salep-mucilage is a horny mass dissolving slowly in water without acid reaction. Hydrolysis converts it quantitatively into *d*-mannose, and the analysis shows it to be a tetrasaccharide of *d*-mannose, $(C_6H_{10}O_5)_4$. Acetic anhydride forms a *tetradeca-acetyl* derivative $C_{24}H_{26}O_3(OAc)_{14}$. Hydrogen peroxide oxidises it to formaldehyde, formic and *d*-mannosaccharic acids, carbon dioxide, and *d*-trihydroxyglutaric acid. The formation of the last compound is to be explained by the ready transformation : dextrose $\rightleftarrows$ lævulose $\rightleftarrows$ mannose observed by Lobry de Bruyn and van Eckenstein (Abstr., 1896, i, 116). One atom of carbon being removed in the oxidation, lævorotatory *d*-trihydroxyglutaric acid is formed.

When the hydrolysis of salep-mucilage is only continued until the solution, on pouring into ether-alcohol, yields a granular precipitate instead of a flocculent one, an intermediate product may be isolated as a light, brilliant white powder, dissolving in water to a neutral solution. The nitric ester, prepared by Will and Lenze's method (Abstr., 1898, i, 227), proved to be a trinitrate of a hexosepolysaccharide, $[C_6H_7O_2(NO_3)_3]_x$, dissolving readily in glacial acetic acid, ethyl acetate, or chloroform. Acetic anhydride forms the octoacetate of a mannobiose, $C_{12}H_{14}O_3(OAc)_8$.

d-Mannose-β-naphthylhydrazone crystallises in slender, white microscopic needles melting at 186—187° (compare Lobry de Bruyn and van Eckenstein, Abstr., 1896, i, 588). C. H. D.

Determination of the Constitution of Amines and other Ammonia Derivatives by aid of Permanganates. ALEXANDER GINZBERG (*Ber.*, 1903, 36, 2703—2709).—Amines and similar compounds, with a few exceptions, such as pyridine and tribenzylamine, readily reduce permanganates, although their molecules do not possess a double linking; this behaviour is doubtless due to the great reactivity of the nitrogen atom. Fifty-one amines, selected from the aliphatic, aromatic, and heterocyclic series, were examined. Permanganates may, however, be employed to determine whether a given amine contains a double linking if the amine be treated with benzenesulphonic chloride and the behaviour of the resulting substituted benzenesulphonamide towards permanganates be then tested. Thus, whilst methylamine, for example, decolorises potassium permanganate, benzenesulphonmethylamide, $SO_2Ph{\cdot}NHMe$, does not. Allylamine was the only unsaturated amine examined; benzenesulphonallylamide decolorises potassium permanganate.

Potassium permanganate is soluble in ethyl acetate containing a trace of water to the extent of 1·5 parts to 1000 parts of water; such a solution may accordingly be used in the case of amides, which are practically insoluble in water. A. McK.

Preparation of Amines by Electrolytic Reduction. PETER KNUDSEN (D.R.-P. 143197).—The products of condensation of aldehydes and amines are in many cases stable in concentrated sulphuric acid solution, even at temperatures above 0°. Such solutions may be electrolytically reduced at low temperatures, lead electrodes and a porous diaphragm being employed. Thus ethylamine may be prepared by the electrolysis of ethylideneimine,? $C_6H_{15}N_3$, in 50 per cent. sulphuric acid at 0° with a current of 25 amperes per litre of cathode solution. Benzylamine is obtained by the reduction of hydrobenzamide in 78 per cent. sulphuric acid at 0° with 20 amperes per litre. The process is also applied to the following preparations: methylamine from hexamethylenetetramine; methylethylamine from trioxymethylene and methylamine; diethylamine from aldehyde-ethylamine; methylbenzylamine from the anhydro-base of benzaldehyde and methylamine; and benzylaniline from benzylideneaniline. C. H. D.

Short Notices. Acetylation of some Unsaturated Amines. W. POTOZKY. **Action of Haloid Compounds of Allyl on Zinc Ethyl Iodide; the Preparation and Isolation of Zinc Ethyl Iodide.** S. GWOSDOFF (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 339—343).—It was shown by Musselius (Abstr., 1900, i, 334) that when heated for half-an-hour in nitrobenzene, acetates of the primary amines yield 87—95 per cent. of the theoretical quantity of the corresponding amide, whilst with the secondary amines only 40—50 per cent. is obtained. Experimenting under similar conditions with the acetates of allylamine, benzylamine, and β-methylhexamethyleneamine, the author finds that these yield 90·39, 95·0, and 88·5 per cent. respectively of the corresponding amides. This method can, hence, also be employed for characterising differently substituted unsaturated amines.

On adding 2 mols. of zinc ethyl iodide to 1 mol. of allyl iodide at a low temperature, the reaction yields partly diallyl and ethyl iodide, according to the equation: $ZnEtI + 2C_3H_5I = C_6H_{10} + EtI + ZnI_2$; no Δ^{α}-amylene is formed, as was expected, but only Δ^{β}-amylene, CHMe:CHEt, whilst ethylene and propylene are evolved. Using either allyl chloride or bromide in place of the iodide, neither diallyl nor ethyl iodide is formed, but a good yield of Δ^{β}-amylene is obtained.

Neither carbon disulphide nor ether can be used as a solvent in the purification of zinc ethyl iodide, which is acted on by these liquids; but crystallisation of the double iodide from its solution in ethyl iodide yields the pure salt. T. H. P.

Synthesis of Choline. MARTIN KRÜGER and PETER BERGELL (*Ber.*, 1903, **36**, 2901—2904. Compare Bode, Abstr., 1892, 806).—Hoffmann's trimethyl-β-bromoethylammonium bromide,

$$CH_2Br\cdot CH_2\cdot NMe_3Br,$$

is readily obtained when trimethylamine dried over lime is passed into a series of 4 tubes containing ethylene bromide heated at 110—120°. Any trimethylamine unabsorbed may be recovered by the addition of a vessel placed in liquid air. The bromide melts at

230—231° and yields a *picrate* melting at 158—159°. It is readily transformed into choline hydrobromide when heated with 2·5 times its weight of water at 160° for 4 hours.

The platinichloride and aurichloride melt at temperatures depending on the rate of heating. The picrate is readily soluble in water or alcohol.

Forty mg. of the base injected subcutaneously cause the death of a mouse in 5 minutes, whereas less than 1 mg. of the hydrochloride causes death in 1—2 minutes. J. J. S.

Study of Betaine. Vl. Staněk (*Zeit. Zuckerind. Böhm.*, 1903, **27**, 479—485).—On heating betaine at 290°, it yields carbon dioxide, a small quantity of a substance possessing an alcoholic odour and giving a faint iodoform reaction, trimethylamine, and about 9 per cent. of an amorphous, humous substance. When heated in a sealed tube at 270—280°, betaine splits up mainly in two ways, yielding glycollic acid and trimethylamine on the one hand, and tetramethylammonium hydroxide and carbon dioxide on the other. Betaine hydrochloride, when heated in a sealed tube at 260—270°, yields carbon dioxide, about 70 per cent. of the quantity of tetramethylammonium chloride calculated from the equation :

$$CO_2H\cdot CH_2\cdot NMe_3Cl = CO_2 + NMe_4Cl,$$

trimethylamine, and humous substances. T. H. P.

New Method of Preparing Glycocholic Acid from Ox-bile. Max Bleibtreu (*Pflüger's Archiv*, 1903, **99**, 187—190).—Uranium acetate is added to bile; this precipitates the pigment, while the bile salts remain in solution. The filtrate is treated with sodium phosphate, which removes excess of uranium salt; this is filtered off and the filtrate treated with ferric chloride; this precipitates the glycocholic acid and leaves the taurocholic acid in solution. The precipitate of iron glycocholate is decomposed with ammonia and ammonium glycocholate is left in solution; addition of uranium nitrate to this solution produces a precipitate of uranium glycocholate from which sodium glycocholate is next obtained in solution by treatment on the water-bath with sodium phosphate. The acid is finally liberated by treatment with hydrochloric acid and ether. The whole process can be completed in a few hours. W. D. H.

New Nitrogenous Constituents of Sugar Residues. Felix Ehrlich (*Zeit. Ver. deut. Zucker-Ind.*, 1903, **571**, 809—829).—In the various processes of the manufacture of beet sugar, the proteid substances undergo decomposition, and the products formed accumulate and hence occur in large quantity in the liquors to which the strontia desaccharification process is applied, and may be to a very large extent separated by crystallisation. In this way, the author has isolated leucine and a new compound, d-iso*leucine*, isomeric with it. *d-iso*Leucine crystallises in shining rods or leaflets, which melt and decompose at 280° when heated in a sealed tube. It has $[\alpha]_D$ +9·74° in water, +36·80° in 20 per cent. hydrochloric acid, and +11·1° in alkali solution at 20°; its *lead* salt is strongly lævo-

rotatory; its *benzoyl* derivative melts at 116—117° and has $[\alpha]_D$ $+26.4°$; the *benzenesulphonic* compound melts at 149—150° and has $[\alpha]_D -12.0°$; and its *phenylcarbimide* melts at 119—120° and has $[\alpha]_D +14.9°$.

An *iso*leucine of the same properties can be isolated from blood-fibrin which has been digested with pancreatic juice, and the author considers this to be identical with the above product, which he regards as a β-amino-acid.

Tyrosine appears to be destroyed during the processes of manufacture, since it cannot be detected in the molasses residues. T. H. P.

Preparation of Glutamic Acid from the Waste Liquors from Molasses. KARL ANDRLÍK (*Zeit. Zuckerind. Böhm.*, 1903, **27**, 665—667).—Pure glutamic acid may be prepared from the waste liquors from molasses by treating them with sulphuric (or tartaric or phosphoric) acid and alcohol and separating the alkali sulphate by precipitation with alcohol. Details of this method of preparation are given. T. H. P.

Thiocyanates of Silver and Potassium and their Solubility. By HARRY W. FOOTE (*Amer. Chem. J.*, 1903, **30**, 330—339).—A method has been devised for ascertaining the double salts formed by two single salts with a common ion. It is shown on the basis of the laws regulating the solubility of two salts with a common ion that if the undissolved residue contains two separate salts, its composition will change as the relative proportion of the two salts changes, whilst the composition of the saturated solution remains constant. When, however, only one salt, either single or double, is in the residue, its composition must remain fixed, whilst the composition of the saturated solution varies within certain limits. From these considerations, the rule is obtained that if the composition of the residue varies in different determinations whilst that of the solution remains constant, a mixture of two salts is present; if, on the other hand, the composition of the solution varies whilst that of the residue remains constant, a single salt or one double salt is present.

Experiments have been made with the thiocyanates of silver and potassium. The double thiocyanates have been prepared by Wells and Merriam (Abstr., 1903, i, 155), who described the following compounds: $3KSCN,AgSCN$; $2KSCN,AgSCN$, and $KSCN,AgSCN$. The existence of these three double salts is confirmed. It is shown, however, that the salt $3KSCN,AgSCN$ is unstable at the ordinary temperature, and readily changes into a mixture of the salt

$$2KSCN,AgSCN$$

and potassium thiocyanate; a transition temperature above or below which this salt becomes stable could not be discovered, and it is probable that the unstable salt becomes stable, if at all, only at a low temperature. E. G.

Tetrathiocyanodiamminediaquochromic Acid. RICHARD ESCALES and H. EHRENSPERGER (*Ber.*, 1903, **36**, 2681—2686).—Ammonium tetrathiocyanodiamminechromate (Reinecke's salt)

(compare Werner and Richter, Abstr., 1898, i, 57),

$$Cr[(NH_3)_2(SCN)_4]NH_4,H_2O,$$

prepared by fusing together ammonium thiocyanate and dichromate, gradually loses its water on exposure to sunlight, and changes from bluish-red to violet-white in colour. On decomposing with hydrochloric acid the ammonium salt dissolved in diluted acetone, extracting the product with ether, evaporating, and crystallising from water the residue which is now no longer soluble in ether, small, red spangles of the *acid*, $Cr(NH_3)_2(SCN)_4H,2H_2O$, separate (compare Nordenskiöld, Abstr., 1893, i, 290). The acid which first separates from the ethereal extract seems to be isomeric with this substance, and when exposed to the air loses thiocyanic acid; moreover, from that part of the residue of the ethoreal extract which is insoluble in water, perthiocyanic acid can be extracted by 60 per cent. acetic acid. The two forms of the acid probably have the formulæ $[Cr(NH_3)_2(SCN)_4(OH_2)_2]H$ and $Cr(NH_3)(SCN)_3(OH_2)_2 \cdot NH_3 \cdot HSCN$. W. A. D.

Substituted Halogenated Amides. LUIGI FRANCESCONI and G. DE PLATO (*Gazzetta*, 1903, 33, i, 226—233).—*Chloroacetylbromoamide*, $CH_2Cl \cdot CO \cdot NHBr$, obtained by the action of bromine (rather more than 2 mols.) on mercuriochloroacetamide (1 mol.) in chloroform solution, is deposited in shining, white crystals melting at 61—63°; it is soluble in ether, by which it is decomposed, yielding mainly chloroacetamide; water and benzene also decompose it, but in chloroform the change is very slow.

Chloroacetylchloroamide, $CH_2Cl \cdot CO \cdot NHCl$, prepared in an analogous manner to the above, melts at 68—69° and is very readily soluble in water.

Chloroacetyliodoamide is a very unstable substance and could not be isolated.

Mercuriochloroacetamide, for which Menschutkin and Sermolajew (this Journal, 1871, 150) gave the melting point 170°, is found to redden at 185° and decompose at 190°. T. H. P.

Ureides of the Dialkylacetic Acids. GEBRÜDER VON NIESSEN (D.R.-P. 144431).—Whilst malonic and dimethylmalonic acids condense with carbamide in presence of phosphorus oxychloride to form barbituric and dimethylbarbituric acids (Thorne, Trans., 1881, 39, 545), the reaction takes a different course with diethyl and higher substituted malonic acids, the ureides of dialkylacetic acids being produced according to the equation:

$$CR_2(CO_2H)_2 + CO(NH_2)_2 = CR_2 \cdot CH \cdot CO \cdot NH \cdot CO \cdot NH_2 + CO_2 + H_2O.$$

Other condensing agents may be used in place of phosphorus oxychloride.

β-Ethylbutyrylcarbamide, $C_7H_{14}O_2N_2$, from diethylmalonic acid, crystallises from hot water in needles melting at 207·5° (corr.). Concentrated hydrochloric acid decomposes it at 100° into carbamide and β-ethylbutyric acid. *β-Propylvalerylcarbamide*, $C_9H_{18}O_2N_2$, crystallises from alcohol in colourless needles melting at 192·5° (corr.). *β-Methylbutyrylcarbamide*, $C_6H_{12}O_2N_2$, forms colourless needles and melts at 178·5° (corr.).

When fuming sulphuric acid is employed as the condensing agent, the ureides of the dialkylmalonic acids may be isolated. These pass into dialkylacetylcarbamides when heated.

Ureidodiethylmalonic acid crystallises from hot water in leaflets, passing into β-ethylbutyrylcarbamide at 162°. *Ureidodipropylmalonic acid*, $C_{10}H_{18}O_4N_2$, is precipitated by acids from its solution in alkalis and melts at 146°, passing into β-propylvalerylcarbamide.

C. H. D.

Preparation of *CC*-Dialkylbarbituric Acid. GEBRÜDER VON NIESSEN (D.R.-P. 144432).—The action of alkyl iodides on silver barbiturate gives only a small yield of dialkylbarbituric acids. A good yield is obtained by the action of alkyl bromides or iodides on *C*-alkylbarbituric acids. CC-*Diethylbarbituric acid*, $C_8H_{12}O_3N_2$, crystallises from hot water and melts at 191° (corr.). CC-*Methylethylbarbituric acid*, $C_7H_{10}O_3N_2$, crystallises in flat prisms and melts at 212°.

C. H. D.

Synthesis of Polypeptides. EMIL FISCHER (*Ber.*, 1903, 36, 2982—2992. Compare this vol., i, 465, 607).—*Diglycylglycine*, $NH_2·CH_2·[CO·NH·CH_2]·CO_2H$, formed when chloroacetylglycylglycine is hydrolysed with aqueous ammonia, crystallises in microscopic needles easily soluble in hot water, but sparingly so in cold; when heated, it melts and decomposes at 246° (corr.). It is precipitated from its sulphuric acid solution by phosphotungstic acid as an amorphous mass soluble in excess. The *ethyl ester* is very easily formed when the tripeptide is acted on by alcoholic hydrochloric acid. The hydrochloride melts at 214—219° (corr.) and is very sparingly soluble in alcohol, crystallising in small, rectangular plates. Ethyl chlorocarbonate and alkali convert the tripeptide into the known carbethoxydiglycylglycine.

a-Bromopropionylglycylglycine ester, prepared by the interaction of glycylglycine ester and a-bromopropionyl bromide, crystallises from water in four-sided, oblique plates, sinters at 130°, and melts at 135—136° (corr.).

a-Bromopropionylglycylglycine, $CHMeBr·[CO·NH·CH_2]_2·CO_2H$, crystallises in prisms, melts at 166—167° (corr.), and is soluble in 2 parts of boiling, or 35 parts of cold, water. It is prepared either by hydrolysing the ester, or, better, directly from glycylglycine.

Alanylglycylglycine, $NH_2·CHMe·[CO·NH·CH_2]_2·CO_2H$, formed on heating the preceding compound with aqueous ammonia, melts and decomposes at 214° (corr.). It crystallises in needles and is more soluble than diglycylglycine. Ethyl chlorocarbonate converts it into *carbethoxyalanylglycylglycine*, small, obliquely-cut prisms melting at 161—162° (corr.). *a-Bromo*iso*hexoylglycylglycine ester* crystallises in needles melting at 124—125° (corr.), and is sparingly soluble in water, easily so, however, in hot alcohol. *a-Bromo*iso*hexoylglycylglycine* crystallises in needles melting at 144—145° (corr.). It can be prepared from the ester or directly from glycylglycine. *Leucylglycylglycine*, $CHMe_2·CH_2·CH(NH_2)·[CO·NH·CH_2]_2·CO_2H$, which melts and decomposes at 235° (corr.), is soluble in less than $2\frac{1}{2}$ parts of cold water, and forms

an easily soluble light blue copper salt. *Phenylcarbamidoleucylglycylglycine*, produced by the interaction with phenylcarbimide, crystallises from water in hexagonal plates melting at 182—183° (corr.). *Leucylglycylglycine ethyl ester* forms a hydrochloride melting at 225°, easily soluble in water. The ester is an oil also easily soluble in water. Ammonia converts it into a compound showing a marked biuret coloration, which is probably the corresponding *amide*. E. F. A.

Synthesis of Polypeptides. EMIL FISCHER and ERICH OTTO (*Ber.*, 1903, **36**, 2993. Compare this vol., i, 607).—Carbethoxyglycine ethyl ester and carbethoxyglycine have already been described by Hantzsch and Metcalf (Abstr., 1896, i, 521) as ethyl urethaneacetate and the corresponding acid. E. F. A.

Action of Silver Cyanate on Acyl Chlorides. I. Acetylcarbimide. OTTO C. BILLETER (*Ber.*, 1903, **36**, 3213—3218).—Silver cyanate reacts with acyl chlorides and sulphonic chlorides to form carbimides, nitriles being produced as by-products in the first case, and anhydrides in the second. The reaction with acyl chlorides takes place without heating, that with sulphonic chlorides at 120—140°.

Acetylcarbimide, $CH_3\cdot CO\cdot N\colon CO$, prepared by adding $\frac{1}{3}$ mol. of silver cyanate to 1 mol. of acetyl chloride, distilling, adding more silver cyanate to the distillate, and repeating these operations, is a colourless, limpid liquid of penetrating odour, boiling at 79° under 708 mm. pressure and at 80—80·3° under 737 mm. pressure and having a sp. gr. 1·0892 at 18°/4°. It reacts violently with water or alcohol. Phenol reacts with development of heat, forming *phenylacetylcarbamate*, $NHAc\cdot CO_2Ph$, which crystallises from dilute alcohol in silky needles, melts at 117°, and dissolves in sodium hydroxide. Acetylcarbimide and ethylene glycol form *ethylene acetylcarbamate*, $(NHAc\cdot CO_2)_2C_2H_4$, which crystallises in white, hair-like needles melting at 174°. o-*Phenylene acetylcarbamate*, $(NHAc\cdot CO_2)_2C_6H_4$, from catechol, crystallises in white needles melting at 175°. Benzamide reacts with acetylcarbimide only on warming, forming *benzoylacetylcarbamide*, $C_{10}H_{10}O_3N_2$; this forms colourless, rectangular plates melting at 187°. Phenylhydrazine reacts vigorously, and it is advisable to add ether. The product crystallises in silky, felted needles melting at 184° and dissolving in alkalis, and represented either by $NHPh\cdot N(CO\cdot NHAc)_2$ or $NHAc\cdot CO\cdot NH\cdot NPh\cdot CO\cdot NHAc$. C. H. D.

Action of Iodine on Potassium Ferro- and Ferri-cyanides. J. MATUSCHEK (*Chem. Zeit.*, 1903, **27**, 1000).—When iodine is gradually added to an aqueous solution of potassium ferrocyanide in the dark and a current of air then passed through the solution until the odour (of iodine, hydrogen iodide, and hydrogen cyanide) disappears, the precipitate of Prussian blue can then be removed by filtration. Its formation is represented by $7K_4Fe(CN)_6 + 28I + 12H_2O = 28KI + 24HCN + Fe_4[Fe(CN)_6]_3 + 6O_2$. Iodine does not dissolve so readily in potassium ferricyanide as in potassium ferrocyanide; Prussian blue may also be obtained from the ferricyanide after a solution of the latter has stood in contact with iodine for $6\frac{1}{2}$ months. The action is

thus represented: $7K_6Fe_2(CN)_{12} + 42I + 24H_2O = 2Fe_4[Fe(CN)_6]_3 + 42KI + 48HCN$.

Instead of the iodine acting as represented in these equations, it is more probable that the hydrogen iodide, liberated by the action of iodine on water, acts on the solutions of the complex cyanides.

A. McK.

Normal Propylphosphine. Alfred Partheil and A. Gronover (*Arch. Pharm.*, 1903, **241**, 411).—n-*Propylphosphine*, $CH_2Et \cdot PH_2$, was obtained, along with a small amount of *iso*propylphosphine, by heating *n*-propyl iodide (21 grams) with phosphonium iodide (20 grams) and zinc oxide (5 grams) for 3 hours at 160—170° in a sealed tube. It is a liquid, which boils at 53—53·5°, and inflames in the air.

C. F. B.

Action of Triethylphosphine on Ethylene Chlorohydrin. Alfred Partheil and A. Gronover (*Arch. Pharm.*, 1903, **241**, 409—411).—When triethylphosphine (1 mol.) is heated with ethylene chlorohydrin (1 mol.) for 2 hours at 150° in a sealed tube filled with carbon dioxide, *hydroxytetra-ethylphosphonium chloride*,

$$OH \cdot CH_2 \cdot CH_2 \cdot PEt_3Cl,$$

is obtained; this and the *hydroxide*, obtained from it by treatment with moist silver oxide, both form white, hygroscopic, crystalline masses; the hydroxide is interesting on account of its structural analogy with choline, $OH \cdot CH_2 \cdot CH_2 \cdot NMe_3 \cdot OH$. The *platinichloride*, *aurichloride*, and *mercurichloride* with $1HgCl_2$ were analysed; they melt at 221—222°, 171—172°, and 164° respectively. C. F. B.

Amphoteric Character of Cacodylic Acid. Jan von Zawidzki (*Ber.*, 1903, **36**, 3325—3337).—The acid character of cacodylic acid is so slightly marked that it does not form salts with ammonia; it combines, however, with strong acids. Since cacodylic acid can be estimated by titration with baryta or sodium hydroxide using phenolphthalein as indicator, it follows that its salts, with the metals of the alkalis and alkaline earths, undergo practically no hydrolytic dissociation. This conclusion is confirmed by determinations of the electrical conductivity of sodium and barium cacodylates. The dissociation constant of cacodylic acid is $4 \cdot 2 \times 10^{-7}$, about the same value as that of carbonic acid ($k = 3 \cdot 2 \times 10^{-7}$) and phenol ($k = 5 \cdot 0 \times 10^{-7}$), a result which is contradictory to the behaviour of cacodylic acid when titrated against strong bases with phenolphthalein as indicator. This abnormal behaviour cannot be attributed to the presence of anhydride in aqueous solutions of cacodylic acid, since cryoscopic determinations show that cacodylic acid in aqueous solution possesses the normal molecular weight. Cacodylic acid must, therefore, be an amphoteric electrolyte (compare Winkelblech, Abstr., 1901, ii, 370) or a pseudo-acid.

The electrical conductivity of aqueous solutions of hydrochloric or of nitric acids is considerably diminished by the addition of equivalent quantities of cacodylic acid. The dissociation constant of cacodylic

acid as a base is also found to be $4 \cdot 05 \times 10^{-13}$. The basic character of cacodylic acid is therefore somewhat stronger than that of dimethylpyrone and weaker than that of betaine.

The presence of hydroxyl ions in aqueous solutions of cacodylic acid was also proved by the accelerating effect exercised by cacodylic acid on the bi-rotation of dextrose. From the experiments quoted, the dissociation constant of cacodylic acid as a base is $2 \cdot 47 \times 10^{-13}$.

Cacodylic acid is shown to be neither a pseudo-acid nor a pseudobase, since the influence of temperature on the dissociation constant of cacodylic acid, either as an acid or as a base, is exceedingly slight.

Cacodylic acid is a typical amphoteric electrolyte. One of Hantzsch's criteria for pseudo-acids, namely, the absence of hydrolysis in the case of alkali salts of feebly-conducting acids, applies not only to pseudoacids, but also to many amphoteric electrolytes. A. McK.

Chemical Rôle of Catalysts. I. NICOLAI D. ZELINSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 399—404).—The monochlorides of the naphthene hydrocarbons do not react with magnesium and ether either alone or in presence of carbon dioxide, but if there be present also traces of iodine, of a magnesium organic compound such as magnesium methyl iodide, of free hydriodic acid, or of an aluminium haloid salt, the reactions proceed readily and often violently. Further, magnesium and iodine do not act either alone or when in benzene or carbon disulphide solution, but only when ether is present. The reaction then proceeds violently with a deposition of colourless prisms melting at about 50°; according to the author, this compound is an intermediate product and a *derivative* of diethyloxonium hydroxide having the constitution $Mg(OEt_2I)_2$.

When hydrogen iodide is passed over magnesium and ether, no reaction takes place at first, but crystals having the same composition as the foregoing compound are formed later.

Bromine, magnesium, and ether yield a liquid *compound*, $MgBr_2,3Et_2O$, which, when kept over sulphuric acid, gives a solid, crystalline *compound* having the composition $MgBr_2,Et_2O$.

The energetic action of magnesium and iodine on alcohols is due to the formation of a compound, OMe·MgI.

The influence of the intermediate diethyloxonium derivative in bringing about the action between naphthene chloride, magnesium, and ether is due to the small amount of heat developed in its formation.

T. H. P.

Monomethyl Tin Compounds. II. PAUL PFEIFFER and R. LEHNARDT (*Ber.*, 1903, 36, 3027—3030. Compare this vol., i, 470, and Pope and Peachey, this vol., i, 741).—*Methylstannic chloride*, $SnMeCl_3$, prepared by the action of hydrogen chloride on methylstannonic acid, separates from light petroleum in large, colourless, transparent prisms, melts at 43°, fumes in the air, and soon liquefies; it is suggested that the compound, melting at 105—107°, described by Pope and Peachey is perhaps dimethylstannic chloride, $SnMe_2Cl_2$, as

its boiling point and melting point are abnormally high for the monomethyl compound.

Basic *methylstannic sulphate*, $OH\cdot SnMeSO_4,xH_2O$, prepared by dissolving methylstannonic acid in 50 per cent. sulphuric acid, separates as a heavy, crystalline, white powder, dissolves slowly in water, and is left as a glassy mass on evaporating the solution; it is insoluble in alcohol, but cannot be precipitated by adding alcohol to its aqueous solution.

Methylstannic sulphide, $(SnMe)_2S_3$, prepared by the action of hydrogen sulphide on the iodide, is a white precipitate, soluble in ammonium sulphide but insoluble in water and organic solvents.

Dimethylstannone, $SnMe_2O$, prepared by acting on an alkaline solution of stannous chloride with methyl iodide and passing carbon dioxide into the solution until the odour of $SnMe_3\cdot OH$ can be detected, is obtained in flaky crystals, and can be purified by converting into the bromide, $SnMe_2Br_2$, and decomposing the latter by warming with ammonia water. T. M. L.

Cyclic Compounds. Heptanaphthylene, its Chlorohydrin, Oxide, and Chloroketone. Structure of the Heptanaphthylenes. WLADIMIR B. MARKOWNIKOFF and GEORGE STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 389—399).—With the exception of α-(or 1 : 2-)naphthylene [1-methyl-$\Delta^{1\cdot 2}$-*cyclo*hexene] (see Markownikoff and Tcherdintzeff, Abstr., 1900, i, 578), all the heptanaphthalenes at present known consist of mixtures of isomeric compounds. The authors have now prepared 1-methyl-$\Delta^{3\cdot 4}$-*cyclo*hexene in a pure state by heating the *xanthogenic ester* of 1-*methyl*cyclo-2-*hexanol*, $CS_2Me\cdot O\cdot C_7H_{13}$, which is obtained by the action of carbon disulphide and methyl iodide on the sodium derivative of 1-methyl*cyclo*-2-hexanol in xylene solution and is a viscous, faintly yellow, unpleasant smelling liquid boiling and decomposing at 149—151° under 18 mm. pressure; it has a sp. gr. 1·0825 at 20°/20° and 1·084 at 15°/15° and $[\alpha]_D$ 29°5′.

1-*Methyl*-Δ-$^{3\cdot 4}$-cyclo*hexene*, $CHMe{<}{\begin{smallmatrix}CH_2-CH\\CH_2\cdot CH_2\end{smallmatrix}}{>}CH$, boils at 101·9° under 753 mm. pressure, has $[\alpha]_D$ +110° at 20°, a sp. gr. 0·8207 at 0°/0°, 0·8003 at 20°/20°, 0·8047 at 15°/15°, and 0·7986 at 20°/0°; it has an odour resembling that of the acetylene hydrocarbons and readily absorbs oxygen, its properties being similar to those of its homologues and isomerides. Oxidation by means of nitric acid yields β-methyladipic acid.

The corresponding *chlorohydrin*, $C_7H_{17}Cl\cdot OH$, is a colourless, viscous liquid with an odour recalling that of iodoform; it boils at 116·5—117° under 40 mm. pressure and with slight decomposition at 205—206° under 758 mm. pressure; it has a sp. gr. 1·1224 at 0°/0°, 1·1026 at 20°/20°, and 1·1002 at 20°/0°, and $[\alpha]_D$ +1°11′42″ at 20°; 100 parts of water dissolve 1 part of the hydrocarbon at the ordinary temperature. The chlorohydrin is also obtained by the addition of hydrochloric acid to the oxide (see later), and, as thus prepared, is optically inactive. By heating the chlorohydrin with concentrated aqueous potassium hydroxide, it is converted

into the corresponding *oxide*, $C_7H_{12}O$; this is a fairly mobile liquid which boils at 146° under 735 mm. pressure and has an ethereal odour; it has $[\alpha]_D$ $+24°51'$ at 20° and a sp. gr. 0·9550 at 0°/0°, 0·94102 at 20°/20°, and 0·9396 at 20°/0°; it dissolves slightly in water.

The corresponding *chloro-ketone*, $C_7H_{11}OCl$, obtained by oxidising the chlorohydrin by means of chromic acid, is a liquid which has a sharp smell and boils at 114° under a pressure of 40 mm.; it has feeble ketonic propeities, for it forms no semicarbazide and its sodium bisulphite compound is unstable.

The authors conclude that the higher the boiling point of a heptanaphthylene the lower the optical activity, and that the 1-methyl-$\Delta^{2\cdot3}$-*cyclo*hexene, at present not isolated, should have a boiling point 104° and a specific rotation between 0° and 110° T. H. P.

Hydrocarbons of the *cyclo*Hexadiene Series. ARTHUR W. CROSSLEY and HENRY R. LE SUEUR (*Ber.*, 1903, 36, 2692—2695).—A reply to certain criticisms of Harries and Antoni (this vol., i, 613). That the substance described as 1 : 1-dimethyl-$\Delta^{2\cdot4}$-*cyclo*hexadiene (Trans., 1902, 81, 821) is really such is shown by its yielding on reduction a tetrahydro-derivative which readily absorbs 2 atoms of bromine and is oxidised by permanganate to $\beta\beta$-dimethyladipic acid; the 1 : 1-dimethyl*cyclo*hexadiene, on the other hand, gives *as*-dimethylsuccinic acid under similar conditions. It is suggested that Harries and Antoni's 1 : 1-dimethyl-$\Delta^{2\cdot5}$-*cyclo*hexadiene is more probably 1 : 2-dimethyl-$\Delta^{2\cdot5}$-*cyclo*hexadiene. W. A. D.

Compounds of Aluminium Chloride which act as Ferments in Synthetical Reactions. GABRIEL GUSTAVSON (*J. pr. Chem.*, 1903, [ii], 68, 209—234. Compare Abstr., 1883, 577).—When ethyl chloride reacts on benzene in presence of aluminium chloride, two layers are formed, the upper of which consists of the excess of benzene, the lower of the reaction product, from which benzene, ethylbenzene, and a small amount of diethylbenzene are obtained by distillation or by washing with light petroleum. The residue is an additive compound of aluminium chloride and *s*-triethylbenzene, $Al_2Cl_6,C_6H_3Et_3$, an oily, yellow liquid, distilling almost unchanged at 132—138° under 9 mm. pressure; it is insoluble in light petroleum, and, on addition of water, is decomposed with liberation of *s*-triethylbenzene and a very small amount of *as*-triethylbenzene. The aluminium chloride-triethylbenzene forms additive compounds with benzene and its homologues such as $Al_2Cl_6,C_6H_3Et_3,6C_6H_6$; $Al_2Cl_6,C_6H_3Et_3,5C_7H_8$; $Al_2Cl_6,C_6H_3Et_3,3C_6H_3Me_3$. These compounds are decomposed into aluminium chloride-triethylbenzene and the hydrocarbon added when distilled or washed with light petroleum. The hydrocarbon added does not replace the triethylbenzene, but hydrogen atoms of the triethylbenzene are replaced very slowly by alkyl groups when the aluminium chloride-triethylbenzene is in combination with a homologue of benzene.

Ethyl chloride and bromide react on the hydrocarbon in combina-

tion with aluminium chloride-triethylbenzene, the more easily the fewer the substituting groups already present; this influence of the aluminium chloride-triethylbenzene extends from the hydrocarbon in combination to that present in excess. With an excess of aluminium chloride, the action of ethyl chloride on benzene results almost entirely in the formation of the compound $Al_2Cl_6,C_6H_3Et_3$. The ethyl chloride may be replaced by ethylene in the reaction. Alkylation with an excess of ethyl chloride results finally in the formation of Al_2Cl_6,C_6Et_6, which has the ferment-like properties of the triethylbenzene compound. The compounds Al_2Cl_6,C_6H_5Et and $Al_2Cl_6,C_6H_4Et_2$ cannot be formed from the triethylbenzene compound or by addition of ethyl- or diethyl-benzene to aluminium chloride. The action of ethylbenzene on aluminium chloride in presence of hydrogen chloride takes place with development of heat aud results in the formation of the compound $Al_2Cl_6,C_6H_3Et_3$, benzene, and ethylbenzene.

The action of *iso*propyl bromide on benzene and aluminium bromide at $-8°$ leads to the formation of a crystalline compound $Al_2Br_6,C_6H_3Pr_3^{\beta}$, which forms additive compounds with benzene hydrocarbons. Ethylene dibromide, benzene, and aluminium bromide form a red, crystalline compound, $Al_2Br_6,C_6(C_2H_4)_3$, which combines with hydrocarbons and is decomposed on addition of water with formation of a solid oxygenated product.

When the compound $Al_2Br_6,6C_6H_5Me$ is washed with light petroleum, the residue is a green liquid, probably Al_2Br_6,C_6H_5Me. On distillation, $Al_2Cl_6,6C_6H_5Me$ leaves a green liquid residue which is decomposed by water with the liberation of toluene.

The compound $Al_2Cl_6,C_6H_4Me_2$ is obtained as a liquid by washing with light petroleum the lower layer, which is formed with development of heat by the action of hydrogen chloride on a mixture of aluminium chloride and *m*-xylene. When this compound is distilled at 95—100° under 14 mm. pressure, the greater part decomposes and remains as a residue which, when treated with water, yields benzene, toluene, and hydrocarbons distilling between 140° and 160°. The compound $Al_2Cl_6,C_6H_4Me_2$ has the additive and fermentative properties of $Al_2Cl_6,C_6H_3Et_3$. The additive compounds with hydrocarbons are liquids and are insoluble in excess of the hydrocarbon.

G. Y.

Synthesis of Hydrocarbons by the Aid of Organo-magnesium Compounds. JOSEPH HOUBEN (*Ber.*, 1903, 36, 3083—3086. Compare Werner and Zilkins, this vol., i, 615).—Small amounts of hydrocarbons are formed in the preparation of alkylmagnesium haloids, probably according to the equation $2RBr + Mg = MgBr_2 + R_2$, as they are not formed when an alkyl bromide is brought into contact with an ethereal solution of the alkylmagnesium bromide. If, however, the ether is removed and the alkylmagnesium haloid is heated with an alkyl iodide, reaction occurs and a hydrocarbon is produced: $R{\cdot}MgBr + R'Br = MgBr_2 + R{\cdot}R'$. Methyl sulphate reacts much more readily than methyl iodide. Ethylbenzene has been synthesised by the action of methyl sulphate on an ethereal solution of benzylmagnesium chloride; the yield is some 21 per cent. and dibenzyl is obtained as a

by-product. A 30 per cent. yield of toluene has been obtained from methyl sulphate and phenyl magnesium bromide, and a 68 per cent. yield of *p*-xylene from methyl sulphate and *p*-bromophenylmagnesium bromide. J. J. S.

Allylbenzene and its Homologues. FRANZ KUNCKELL (*Ber.*, 1903, **36**, 3033—3034. Compare this vol., i, 331).—The low boiling point assigned by the author to allylbenzene (167—170° instead of 174—175°) cannot be due to the presence of 15 per cent. of propylbenzene, as Klages has suggested (this vol., i, 688), since these liquids are easily separated by distillation, and the allylbenzene gives a normal yield of the dibromide. T. M. L.

Introduction of a Definite Number of Halogen Atoms into Volatile Organic Compounds. LEO MARCKWALD (D.R.-P. 142939).—In the preparation of halogen derivatives of organic compounds, a certain proportion of more highly halogenised derivatives is usually formed, even in presence of a considerable excess of the original compound. This may be avoided by the addition of fresh material from time to time during the halogenisation, the product being simultaneously removed from the further action of the halogen. A form of apparatus is described, suitable for the chlorination of toluene, acetic acid, &c., at their boiling points. For instance, toluene is distilled, its vapours passing into the chlorinating vessel, which is fitted with a reflux condenser. The chlorinated product siphons back into the distilling vessel, from which the toluene volatilises, to be employed again. By placing a condenser between the distilling and halogenising vessels, the apparatus may be made suitable for chlorination at the ordinary temperature, as in the preparation of chlorobenzene. C. H. D.

Pyrogenetic Reactions by means of the Electric Current. Behaviour of Benzyl Chloride, Benzylidene Chloride, and Benzotrichloride. WALTHER LÖB (*Ber.*, 1903, **36**, 3059—3062. Compare Abstr., 1901, ii, 371; 1902, i, 3; 1903, i, 20, 29).—When the vapours of benzyl chloride, benzylidene chloride, and benzotrichloride are decomposed by a wire heated to redness in an electric current, the behaviour is similar to that previously described in the case of chloroform, that is, the initial change is the dissociation into chlorine (or hydrogen chloride) and a compound of bivalent carbon, which compound immediately polymerises.

Benzyl chloride readily forms stilbene, thus:

$$2CH_2PhCl \longrightarrow 2HCl + 2PhCH;\ 2CHPh \longrightarrow PhCH{:}CHPh.$$

Benzylidene chloride yields a mixture of α- and β-tolane dichlorides, thus: $2CHPhCl_2 \longrightarrow 2CPhCl + 2HCl;\ 2PhCCl \longrightarrow \begin{matrix}PhCCl\\ \Vert\\ PhCCl\end{matrix}$ and $\begin{matrix}PhCCl\\ \Vert\\ ClCPh\end{matrix}$.

With benzotrichloride, the chlorine formed in the initial action is not evolved, but acts on the tolane dichlorides to form tri- and tetra-chlorides, thus: $2PhCCl_3 \longrightarrow 2PhCCl + 2Cl_2;\ 2PhCCl \longrightarrow \begin{matrix}PhCCl\\ \Vert\\ PhCCl\end{matrix} + \begin{matrix}PhCCl\\ \Vert\\ ClCPh\end{matrix}$,

$$\begin{array}{c}PhCCl\\ \| \\ PhCCl\end{array} + \begin{array}{c}PhCCl\\ \| \\ ClCPh\end{array} + 2Cl_2 = \begin{array}{c}PhCCl\\ | \\ PhCCl_2\end{array} + \begin{array}{c}PhCCl_2\\ | \\ PhCCl_2\end{array}.$$

The tolane trichloride formed in this reaction is represented as containing a tervalent carbon atom (compare this vol., i, 811). The isolation of phenylmethylene or of chlorophenylmethylene was not effected. The possibility of isolating those substances was indicated, however, by the fact that, when the *cis*- and *trans*-tolane dichlorides were distilled under atmospheric pressure, they undergo transformation into one another, but are not decomposed; in this transformation, chlorophenylmethylene is probably formed as a dissociation product. Vapour density determinations of the two tolane dichlorides at the temperature of boiling sulphur, mercury, and phosphorous pentasulphide respectively under atmospheric pressure did actually indicate that such a dissociation occurs. A. McK.

Oxidation by means of Ozone. CARL D. HARRIES (*Ber.*, 1903, 36, 2996—2997. Compare this vol., i, 605).—Phenyl iodide is oxidised by ozonised oxygen to iodosobenzene; the formation of the hypothetical intermediate product, iodobenzene, could not be detected.

Aromatic aldehydes, when acted on for some time by ozonised oxygen, are converted into the corresponding acids, thus benzoic acid is formed from benzaldehyde. Aliphatic aldehydes, however, are not attacked under these conditions. E. F. A.

Behaviour of ω-Iodomethyltrimethylene towards Alkali Hydroxides. NICOLAUS I. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 375—381).—The author has attempted to remove hydrogen iodide from ω-iodomethyltrimethylene, $\begin{array}{c}CH_2\\ | \\ CH_2\end{array}\!\!>CH\cdot CH_2I$, by the action of potassium hydroxide and so form the compound $\begin{array}{c}CH_2\\ | \\ CH_2\end{array}\!\!>C{:}CH_2$; he finds, however, that the trimethylene ring breaks down during the reaction yielding erythrene, which was separated as the dibromide, $C_4H_6Br_2$, prepared by Griner (Abstr., 1893, i, 450) and by Thiele (Abstr., 1900, i, 2) or, by using excess of bromine, as tetrabromoerythrene. T. H. P.

***m*-Xylylallylsulphone.** JULIUS TRÖGER and W. HILLE (*J. pr. Chem.*, 1903, [ii], 68, 309—312. Compare Abstr., 1902, i, 776).—If *m*-xylylallylsulphone (previously obtained sometimes as a crystalline mass, sometimes as an oil), is dissolved in aqueous alcohol and the solution allowed to evaporate slowly, it crystallises in yellowish-white, broad needles and melts at 52°. In carbon tetrachloride solution, it combines with chlorine at the ordinary temperature to form the *dichloride*, $C_6H_3Me_2\cdot SO_2\cdot C_3H_5Cl_2$, as a viscid, yellowish-brown oil. When heated with hydrogen bromide at 100°, it forms *m-xylylbromopropylsulphone*, $C_6H_3Me_2\cdot SO_2\cdot C_3H_6Br$, as a brownish-yellow oil, insoluble in water.

The preparation of di-*m*-xylylethylenedisulphone by the action of ethylene bromide on sodium *m*-xylenesulphinate, obtained by reduction of *m*-xylenesulphonic chloride, has been repeated and the product found to melt at 163° (compare Abstr., 1902, i, 775). The *m*-xylenesulphonic acid, from which the product melting at 146° was obtained, was probably impure. G. Y.

Benzenesulphonic Peroxide. RUDOLPH F. WEINLAND and H. LEWKOWITZ (*Ber.*, 1903, 36, 2702—2703).—Whilst organic derivatives of percarbonic acid are known (compare Baeyer and Villiger, Abstr., 1901, i, 62), the corresponding compounds of persulphuric acid have not hitherto been prepared.

Benzenesulphonic peroxide, prepared by shaking benzenesulphonic chloride with an aqueous solution of sodium peroxide at 0°, separates from ether in colourless, flat prisms, which are very unstable, being readily deliquescent and becoming yellow at temperatures over 20°. It is insoluble in water, sparingly soluble in alcohol, and readily so in ether or in chloroform; at 53—54°, it decomposes with a slight explosion. It liberates iodine from a solution of potassium iodide.

A. McK.

p-Toluenesulphinic Acid. II. ERNST VON MEYER (*J. pr. Chem.*, 1903, [ii], 68, 263—293. Compare Abstr., 1901, i, 264).—[With A. HEIDUSCHKA.]—Aminophenyl *p*-tolyl sulphide acquires a bluish-green colour on exposure to air and light, it boils at 365°, and is volatile with steam. The hydrochloride melts at 188·5°; the *platinichloride*, $(C_{13}H_{13}NS)_2,H_2PtCl_6$, crystallises in small, yellow leaflets; the sulphate melts and undergoes slight decomposition at 215°; the *nitrate* forms a white, crystalline mass, acquires a brown colour on exposure to air, and melts at 170°; the *oxalate*, $C_{13}H_{13}NS,C_2H_2O_4$, crystallises in leaflets and melts and forms di-*p*-thiotolyloxanilide at 169°. The *benzoyl* derivative, $C_7H_7\cdot S\cdot C_6H_4\cdot NHBz$, formed by Deninger's method (Abstr., 1895, i, 461), crystallises in small, white needles and melts at 192°. The *acetyl* derivative crystallises in white leaflets and melts at 108°. With ethyl oxalate, aminophenyl *p*-tolyl sulphide forms *ethyl* p-*thiotolylphenyloxamate*, $C_7H_7\cdot S\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2Et$, which crystallises in yellow leaflets, melts at 121°, is soluble in the usual organic solvents, and, with alcoholic ammonia, yields p-*thiotolylphenyloxamide*, which crystallises in white needles and melts at 222°.

Di-p-*thiotolyloxanilide*, $(C_7H_7\cdot S\cdot C_6H_4\cdot NH)_2C_2O_2$, formed by fusing together ethyl *p*-thiotolylphenyloxamate and aminophenyl *p*-tolyl sulphide, is obtained as a glistening, crystalline powder, which melts at 242°. The action of ethyl chlorocarbonate on aminophenyl *p*-tolyl sulphide leads to the formation of *ethyl* p-*thiotolylphenylcarbamate*, which crystallises in colourless plates, melts at 94°, and is soluble in alcohol, ether, or light petroleum.

p-*Thiotolylphenylcarbamide* crystallises in colourless needles, melts at 168°, and is soluble in alcohol, ether, or glacial acetic acid. p-*Thiotolyldiphenylcarbamide*, $C_7H_7\cdot S\cdot C_6H_4\cdot NH\cdot CO\cdot NHPh$, formed by the action of phenylcarbimide on aminophenyl *p*-tolyl sulphide, crystallises

from alcohol in matted needles and melts at 190°; when crystallised from pyridine, it melts at 187°. *Di-*p-*thiotolylphenylthiocarbamide* crystallises in glistening leaflets and melts, when freshly prepared, at 155°; six months after preparation, the substance melted at 174°.

With the exception of *trichloroethylideneaminophenyl* p-*tolyl sulphide*, $CCl_3{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}S{\cdot}C_7H_7$, which melts at 107—109° and is formed in small amount by the action of chloral hydrate, no products could be obtained by the action of fatty aldehydes on aminophenyl *p*-tolyl sulphide; the following compounds are obtained by the action of aromatic aldehydes. *Benzylideneaminophenyl* p-*tolyl sulphide*,

$$CHPh{:}N{\cdot}C_6H_4{\cdot}S{\cdot}C_7H_7,$$

crystallises in glistening, white leaflets, melts at 99°, and is easily soluble in alcohol or ether. The o-*hydroxybenzylidene* derivative crystallises in orange-yellow leaflets and melts at 114°; the p-*hydroxybenzylidene* derivative crystallises in flat, yellow needles and melts at 185·5°; the p-*methoxybenzylidene* derivative forms long, yellow needles and melts at 119°; the m-*nitrobenzylidene* compound crystallises in glistening, yellow leaflets and melts at 115°; the p-*nitrobenzylidene* derivative forms glistening, scarlet leaflets and melts at 109°; the p-*chlorobenzylidene* compound forms glistening, yellow leaflets and melts at 138°. *Piperonylideneaminophenyl* p-*tolyl sulphide* crystallises in small, yellow needles and melts at 95°; *cinnamylideneaminophenyl* p-*tolyl sulphide* forms yellow needles and melts at 118°. These aldehyde derivatives are hydrolysed by boiling water or by acids.

Diazotised aminophenyl *p*-tolyl sulphide and resorcinol form a *dye*, $C_7H_7{\cdot}S{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH)_2$, which is obtained as a dark brown, sandy powder, and, in an alkaline-bath, dyes silk a deep orange; the colour is fast to neither light nor acids. With R-salt, diazotised aminophenyl *p*-tolyl sulphide forms a reddish-brown *dye*,

$$C_7H_7{\cdot}S{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(OH)(SO_3H)_2,$$

which dyes silk a light, wool a dark, cherry-red; the colour is neither light nor alkali fast.

Benzenediazoaminophenyl p-*tolyl sulphide* forms a yellow, crystalline powder, melts at 85°, is soluble in alcohol or ether, explodes if quickly heated, and evolves nitrogen when boiled with hydrochloric acid. p-*Nitrobenzenediazoaminophenyl* p-*tolyl sulphide* crystallises in brownish-yellow leaflets and melts at 166°.

Oxidation of acetaminophenyl *p*-tolyl sulphide with fuming nitric acid leads to the formation of p-*tolylacetylanilinosulphoxide*,

$$C_7H_7{\cdot}SO{\cdot}C_6H_4{\cdot}NHAc,$$

which crystallises in small, yellow leaflets and melts at 182·5°. p-*Tolylsulphonoacetanilide*, $C_7H_7{\cdot}SO_2{\cdot}C_6H_4{\cdot}NHAc$, formed by oxidation of the sulphide with potassium permanganate, crystallises in small, colourless needles and melts at 195°.

Aminophenyl *p*-tolyl sulphide combines slowly with methyl iodide to form *aminophenyl*-p-*tolylmethylsulphine iodide*, which crystallises in glistening, brownish-yellow leaflets, melts at 80°, and forms a blue precipitate with silver nitrate in alcoholic solution.

[With Ernst Meyer.]—p-*Tolyl* o-*amino*-m-*tolyl sulphide*, formed by heating *o*-toluidine *p*-toluenesulphinate, crystallises in clusters of

brown, flat needles and prisms, melts at 48—49°, gives the *iso*nitrile reaction with alcoholic potassium hydroxide and chloroform, and yields an odour resembling quinone when oxidised with potassium dichromate and sulphuric acid or with ferric chloride. The *hydrochloride* is a white, crystalline powder and melts at 212°; the *platinichloride* is a brownish-yellow powder; the *sulphate*, $(C_{14}H_{15}NS)_2,H_2SO_4$, crystallises in glistening, rose-coloured leaflets and melts at 191°; the *oxalate* forms rose-coloured needles, melts at 128°, and, when heated above its melting point, forms dithiotolyl-*o*-tolyloxamide; the *picrate* crystallises in glistening, golden-yellow needles and melts at 210°. The *acetyl* derivative, $C_{14}H_{13}S\cdot NHAc$, crystallises in colourless, transparent prisms or plates, melts at 135—136°, and is easily soluble in hot acetone, alcohol, or glacial acetic acid; the *benzoyl* derivative crystallises in colourless prisms and melts at 133°.

Ethyl p-*thiotolyl*-o-*tolyloxamate*, formed by the action of ethyl oxalate on the base, crystallises in colourless, transparent, six-sided plates and melts at 113—114°. p-*Thiotolyl*-o-*tolylphenyloxamide*,

$$C_{14}H_{13}S\cdot NH\cdot CO\cdot CO\cdot NHPh,$$

formed by the action of aniline on the ethyl oxamate, crystallises in glistening, white, flat needles and melts at 238°. *Di*-p-*thiotolyl*-o-*tolyloxamide*, $C_{14}H_{13}S\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_{14}H_{13}S$, obtained by heating the base with its ethyl oxamate, crystallises in glistening, white leaflets and melts at 198—199°. *Ethyl* p-*thiotolyl*-o-*tolylcarbamate* crystallises in long, colourless prisms and melts at 81°. p-*Thiotolyl*-o-*tolylcarbamide* crystallises in glistening, white, flat needles and melts at 175°. p-*Thiotolyl*-o-*tolylphenylcarbamide* forms white needles and melts at 187°. *Di*-p-*thiotolyl*-o-*tolylthiocarbamide* crystallises in slender, white needles and melts at 151°. p-*Thiotolyl*-o-*tolylphenylthiocarbamide* crystallises in transparent prisms or white needles and melts at 143°.

p-Tolyl *o*-amino-*m*-tolyl sulphide itself does not react with aromatic aldehydes, but its hydrochloride, in boiling alcohol or glacial acetic acid solution, forms the hydrochlorides of the aldehyde condensation products. The *benzylidene hydrochloride*, $CHPh{:}N\cdot C_{14}H_{13}S,HCl$, crystallises in prisms and melts at 204°; the *salicylidene hydrochloride*, $OH\cdot C_6H_4\cdot CH{:}N\cdot C_{14}H_{13}S,HCl$, forms golden-yellow needles and melts at 203°; the *cinnamylidene hydrochloride* crystallises in scarlet leaflets and melts at 171°; the *vanillylidene hydrochloride* crytallises in white to violet needles and melts at 200°; the *piperonylidene hydrochloride* crystallises in slender, yellow needles and melts at 210°.

m-*Toluidine* p-*toluenesulphinate* crystallises in rose-coloured needles and melts at 119°. When heated gradually to 240°, it yields m-*toluidine* p-*toluenesulphonate*, which crystallises in white needles or short, thick prisms and melts at 161°, and p-*tolyl* m-*amino*-o-*tolyl sulphide*, obtained as the *hydrochloride*, which crystallises in red needles, or the *sulphate*, which forms red leaflets and melts at 196°.

The action of ethyl oxalate on the base leads to the formation of *di*-p-*thiotolyl*-m-*tolyloxamide*, which crystallises in glistening, white leaflets and melts at 207°, and *ethyl* p-*thiotolyl*-m-*tolyloxamate*, which crystallises in prisms or needles and melts at 113°.

p-*Thiotolyl*-m-*tolylphenylcarbamide* crystallises in white to rose-

coloured needles and melts at 227°. p-*Thiotolyl*-m-*tolylphenylthiocarbamide* crystallises from alcohol, acetone, or benzene and melts at 147°.

G. Y.

Tervalent Carbon. WALTHER LÖB (*Ber.*, 1903, 36, 3063—3067. Compare Abstr., 1902, i, 3, and this vol., i, 806).—Blank's ditolane hexachloride (Abstr., 1889, 261) is considered by the author to be identical with tolane trichloride, and the latter is supposed to be a compound containing tervalent carbon on the following grounds.

The so-called ditolane hexachloride is prepared by warming an alcoholic solution of tolane tetrachloride with zinc dust, a mode of formation which may be compared to Gomberg's preparation of triphenylmethyl. By further action of zinc dust, tolane dichloride is formed. The action is represented by the equations: $CPhCl_2\cdot CPhCl_2 + zn = znCl + CPhCl\cdot CPhCl_2$, $CPhCl\cdot CPhCl_2 + zn = znCl + CPhCl\colon CPhCl$.

The formation of Blank's hexachloride by warming the dichloride with the tetrachloride is best accounted for by the author's idea of the dissociation of the two latter substances, the dissociated products then uniting to form the trichloride.

The formation of Blank's compound by treatment of the dichlorides with chlorine, and the difficulty with which the former is converted into the tetrachloride, is also discussed. The fact that, by the distillation of Blank's compound, hydrogen chloride and the dichlorides are formed, and not the stable tetrachloride, is adduced by the author as an additional argument. Further, the melting point of Blank's substance is 150°, whilst the tetrachloride melts at 163° and the dichlorides at 63° and 143° respectively. Finally, Blank has himself shown by molecular weight determinations that his hexachloride, in benzene solution, has half the calculated molecular weight.

A. McK.

Dibenzylideneacetone and Triphenylmethane. ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1903, 36, 2774—2796. Compare Abstr., 1902, i, 380, 769).—Tri-*p*-nitrotriphenylmethane may be nitrated with fuming nitric acid and sulphuric acid, forming 2 : 4 : 2′ : 4′ : 2″ : 4″-*hexanitrotriphenylmethane*, which crystallises from acetone in almost colourless, six-sided tablets, melting and decomposing at 260°, and dissolving in nitric acid, the solution, when allowed to evaporate over soda-lime, depositing large, six-sided, amber tablets of a *compound*,

$$C_{19}H_{10}O_{12}N_6,HNO_3.$$

After a time, the crystals become turbid, and the nitric acid thus appears to play the part of water of crystallisation. The solubility of nitro-compounds in nitric acid is probably to be explained in other cases by the formation of similar compounds. Alcoholic ammonium sulphide reduces the hexanitro-compound to *tri*-p-*aminotri*-o-*nitrotriphenylmethane*, precipitated by water from acetic acid as orange crystals, becoming dark at 300° without melting, and dissolving in acetone or pyridine. The solution in mineral acids is colourless. The constitution follows from analogy with the reduction of 2 : 4-dinitrotoluene. Tin and hydrochloric acid reduce it to a colourless base, probably hexa-aminotriphenylmethane.

A number of *o*-aminoleuco-bases have been described, but are in many cases wrongly named in the works of reference, and are now corrected. Tetramethyldi-*p*-aminobenzhydrol condenses with *p*-toluidine, forming *2-amino-5-methyl-leucomalachite-green*, crystallising from alcohol-benzene in colourless leaflets melting at 187·5°. The *urethane* crystallises from alcohol in quadratic prisms melting at 158—159°. Manganese dioxide oxidises it at a low temperature to the *urethane* of *2-amino-5-methylmalachite-green*, colourless, rhombic tablets melting and decomposing at 170—172°, dissolving in acids to colourless solutions becoming green only on warming. Hydrolysis is best effected by means of barium hydroxide and pyridine, the *2-amino-5-methylmalachite-green* is precipitated by methyl alcohol as colourless, hexagonal tablets, decomposing at about 200°. The acetic acid solution becomes blue on warming, mineral acids form a green, fluorescent compound, probably of the acridine series. The compound prepared by Fischer and Schmidt (Abstr., 1884, 1315) by oxidation of *o*-acetylaminoleucomalachite-green is shown to be *anhydro-*o*-acetylaminomalachite-green*, $C_{25}H_{27}ON_3$.

The *urethane* of o-*aminoleucomalachite-green* crystallises from methyl alcohol in thick tablets melting at 131—132°, passing on fusion into a modification crystallising in needles and melting at 149°. Lead peroxide oxidises both forms to *o-aminomalachite-green urethane ethyl ether*, separating from alcohol in colourless needles melting at 161—162°, and converted into the *urethane anhydride*, melting at 172—174°, by dissolving in acetic acid and precipitating with sodium carbonate. Barium hydroxide and pyridine hydrolyse it to o-*aminomalachite-green*, crystallising from alcohol in colourless leaflets which melt and decompose at 160°.

[With RICHARD HALLENSLEBEN.]—*Phenyldi*-p-*anisylcarbinol* (*di*-p-*methoxytriphenyl carbinol*), prepared by the oxidation of phenyldi-*p*-anisylmethane (Abstr., 1902, i, 768) with moist lead peroxide, crystallises from ether-light petroleum in short prisms melting at 76—77°. Its solution in glacial acetic acid is orange-coloured, becoming dark red on addition of mineral acids.

Dry hydrogen chloride converts it into *phenyldi*-p-*anisylchloromethane* (*di*-p-*methoxytriphenylchloromethane*), $C_{21}H_{19}O_2Cl$, crystallising from ether in colourless needles melting at 114—115° and forming crystalline double salts with metallic chlorides. Potassium acetate and glacial acetic acid regenerate the carbinol. *Phenylhydrazine* reacts with the carbinol to form *phenyldi*-p-*anisylmethaneazobenzene*, $C_{27}H_{24}O_2N_2$, separating from ether-alcohol in golden crystals melting at 112°. Sodium hydrogen sulphite converts the carbinol into *sodium phenyldi*-p-*anisylmethanesulphonate*, $C_{21}H_{19}O_5SNa,H_2O$. *Triphenylmethylphenylsulphone*, $C_{25}H_{20}O_2S$, from triphenylmethylchloromethane and sodium benzenesulphinate, forms silvery leaflets which melt at 175—176°. *Phenyldi*-p-*anisylmethylphenylsulphone* forms colourless prisms melting at 160—161°. The sulphones crystallise readily, and are suitable for the characterisation of difficultly crystallisable carbinols. Diphenyl-*p*-anisylchloromethane (*p*-methoxytriphenylchloromethane) crystallises from ether in colourless prisms melting at 124°. The corresponding carbinol is reduced by zinc dust and acetic acid to diphenyl-*p*-anisyl-

methane, melting at 64—65° (compare Bistrzycki and Herbst, this vol., i, 639). *Diphenyl*-p-*anisylmethaneazobenzene* crystallises from ether-alcohol in bright yellow needles melting and decomposing at 115°. *Sodium diphenyl*-p-*anisylmethanesulphonate* dissolves readily in alcohol or hot water. *Diphenyl*-p-*anisylmethylphenylsulphone*, groups of needles, melts at 165—166°.

[With Richard Hallensleben.]—Boiling dilute sulphuric acid converts phenyldi-*p*-anisylcarbinol into benzaurin. In similar manner, diphenyl-*p*-anisylcarbinol is converted into *p*-hydroxytriphenylcarbinol, which is converted by heat into diphenylquinomethane, $CPh_2{\cdot}C{:}C_6H_4{:}O$. Both the carbinol and the quinone react with sodium hydrogen sulphite to form *sodium* p-*hydroxytriphenylmethanesulphonate*, $C_{19}H_{15}O_4SNa,3\frac{1}{2}H_2O$. Magnesium methyl iodide reacts with the quinone forming p-*hydroxytriphenylethane*, $CPh_2Me{\cdot}C_6H_4{\cdot}OH$, needles melting at 119—120° and dissolving in sodium hydroxide.

p-Aminobenzophenone reacts with phenyl magnesium bromide dissolved in ether to form *anhydro*-p-*aminotriphenylcarbinol*, $C_{19}H_{15}N$, probably an internal imide or a quinoneimide. Molecular weight determinations yielded no decisive result. Similar experiments have been undertaken with rosaniline. C. H. D.

Reduction of Nitro-compounds to Amines. Johannes Kunz (D.R.-P. 144809).—Sodium disulphide, Na_2S_2, prepared by dissolving sulphur in a boiling solution of sodium sulphide, readily reduces nitrobenzene and its homologues to the corresponding amines, $XNO_2 + H_2O + Na_2S_2 = XNH_2 + Na_2S_2O_3$. The reaction is complete on boiling, and after mechanical separation of the amine the sodium thiosulphate is recovered by evaporation and crystallisation. Mono- or polysulphides are not applicable. C. H. D.

Some By-products from the Manufacture of Aniline. Felix B. Ahrens and Waldemar Blümel (*Ber.*, 1903, **36**, 2713—2716).—The oil examined, which was a by-product from the so-called dry distillation of aniline, was fractionated, when the greater portion distilled between 125° and 160°. The higher fractions, those boiling from 170° onwards, could be nitrated almost completely, whilst the nitration of the lower fractions indicated the presence of aliphatic compounds. Chlorobenzene and iodobenzene were isolated from the aromatic fractions; the mixture of aliphatic and aromatic derivatives was separated by sulphonation of the latter, after which *methyl α-methylbutyl ketone* was isolated; this boiled at 146—147° and had an odour of peppermint. The mother liquor, left after removal of the sodium bisulphite compound of methyl α-methylbutyl ketone, yielded a *ketone* having the formula $C_6H_{12}O$ (b. p. 145—147°) and giving a *nitroso*-derivative. When oxidised by potassium permanganate, it formed mainly propionic acid, but traces of butyric and acetic acids were also detected. A. McK.

Influence of Catalysts on the Formation of Anilides and Amides. Nicolai A. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 343—358).—In order to extend the analogy existing between the

formation of esters from acids and alcohols and the formation of anilides and amides from amines and acids, the author has studied the action of catalysing agents on the speed of the latter reaction.

In the case of the anilides, 4 mols. of the amine and 1 mol. of acetic acid were taken, the excess of amine being employed to diminish the auto-catalysing influence of the acetic acid; the mixture was heated at a temperature of 182°. The amines experimented on were aniline and *o*- and *m*-toluidines, and, as catalysing agents, the hydrogen haloids were employed in the form of salts of the various amines. The accelerating actions of equal quantities of these acids are in the order hydrochloric, hydrobromic, and hydriodic acids, but if the increase of speed of the reaction is referred to equal numbers of ions, then the above order is reversed, so that hydriodic acid exerts the greatest influence. It is found that the ions of the haloid salts of tetra-alkylammonium bases have no accelerating influence on the formation of anilides.

The speed of formation of amides is unaffected by the presence of the halogen hydracids; this result might have been expected since at the temperature at which the reaction takes place the ammonium haloids are not decomposed into ammonia and free acid, and it is to the latter that the catalysing action is due.

Catalysts change only the absolute speeds of reactions and not their relative speeds, which are determined by the structures of the hydrocarbon chains of the organic compounds. T. H. P.

Cyclic *iso*Nitriles and their Derivatives. V. ALEXANDER P. SABANÉEFF and E. RAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 461—466. Compare Abstr., 1901, i, 695, and 1902, i, 604).—Dithio-oxanil (*loc. cit.*) is best prepared by the following method: a solution of 62 grams of potassium hydroxide in 340 c.c. of absolute alcohol is added gradually to a mixture of 23·6 c.c. of acetylene tetrabromide and 40 c.c. of aniline, which is meanwhile kept cool; when all action ceases, 56 grams of flowers of sulphur are added gradually to the cooled solution, which is then either heated to boiling on the water-bath or left overnight and afterwards diluted with 1800 c.c. of water and immediately filtered. The dithio-oxanil is precipitated from the filtrate by means of carbon dioxide or very dilute hydrochloric acid, washed with methyl alcohol and ether, and carefully dried in a desiccator at the ordinary temperature. As thus obtained, dithio-oxanil is a yellow powder which melts at 128—129° if slowly, or at 140° if quickly, heated. It is stable in the dry state and dissolves to a slight extent in methyl or ethyl alcohol, ether, or benzene, and more readily in chloroform or carbon bisulphide; in these solutions, however, resinous products very readily form. It reacts readily with ammonia and both aliphatic and aromatic amines, yielding products to be described later.

On heating with copper, electrolytically deposited and reduced in a current of hydrogen, dithio-oxanil loses sulphur, the resulting *iso*nitrile then undergoing isomeric change into the nitrile, $C_6H_5{\cdot}C{\lessgtr}\genfrac{}{}{0pt}{}{N}{\overset{\|}{C}}$, which afterwards solidifies, forming dicyanostilbene, $CN{\cdot}CPh{:}CPh{\cdot}CN$.

From the results of this and their previous work (*loc. cit.*) and of that of other observers, the authors conclude that, under certain conditions, the *iso*nitriles react with water yielding glycollic acid and an amine: $C_2NPh + 3H_2O = OH \cdot CH_2 \cdot CO_2H + NH_2Ph$, whilst, under similar conditions, nitriles give a substituted glycollic acid and ammonia: $C_2NPh + 3H_2O = OH \cdot CHPh \cdot CO_2H + NH_3$, mandelic acid nitrile being in some cases formed as an intermediate product. Experiments made with a view to removing water from mandelic acid nitrile and so form a cyclic nitrile have as yet met with no success.

T. H. P.

Phenylbutene. CARL D. HARRIES and ALFRED S. DE OSA (*Ber.*, 1903, 36, 2997—3002).—*γ-Amino-α-phenylbutane*, formed by the reduction of benzylideneacetoxime with sodium, is sparingly soluble in water, boils at 101—102° under 14 mm. or at 221—222° under 750 mm. pressure, has a sp. gr. 0·9298 at 20°/20°, and n_D 1·5152. The *hydrochloride* melts at 142—143°, the *oxalate* at 110—112°, and the *acid phosphate* at 172°.

γ-Ureido-α-phenylbutane, produced by interaction with potassium cyanate, crystallises from water in white prisms melting at 119·5°. *γ-Benzoylamino-α-phenylbutane* crystallises in white needles and melts at 108°. Two isomeric *phenylbutenes* are formed on dry distillation of the acid phosphate in a stream of carbon dioxide. The mixture distils between 69° and 73° under 12 mm. pressure; the main portion, which passes over at 71°, has a sp. gr. 0·8954 at 19·5°/19·5°, 0·8892 at 24°/24°, and n_D 1·52085. A white, crystalline *nitrosite*, $C_{10}H_{12}O_3N_2$, decomposing when heating at 110°, can be obtained in small quantities, and is presumably derived from the less abundant isomeride. On oxidation with ozone, benzaldehyde and hydrocinnamaldehyde are formed.

γ-Amino-α-phenyl-Δ^α-butene (2), $CHPh{:}CH \cdot CHMe \cdot NH_2$, is produced when benzalacetoxime is reduced with zinc dust and acetic acid. It boils at 119° under 12 mm. pressure; the *oxalate* melts at 120—122°, the *benzoyl* compound, which crystallises from alcohol in stellar aggregates of needles, at 136—137°, and the additive bromine compound at 169—170°.

E. F. A.

Action of 1-Chloro-2:4-dinitrobenzene on Bases. FRITZ REITZENSTEIN (*J. pr. Chem.*, 1903, [ii], 68, 251—262. Compare Leymann, Abstr., 1882, 1057).—The presence of zinc chloride is not necessary to the formation of substituted diphenylamines by the action of chloro-2:4-dinitrobenzene on secondary aromatic amines, the reaction taking place when these substances are heated together on a water-bath. With tertiary amines alone, chloro-2:4-dinitrobenzene either does not react or forms additive compounds (compare Romburgh, Abstr., 1889, 146; Petermann, *Diss. Marburg*, 1896; Vongerichten, Abstr., 1900, i, 51).

The *additive* compound of *p*-tetramethyldiaminodiphenylmethane and chloro-2:4-dinitrobenzene, $C_{23}H_{25}O_4N_4Cl$, separates from aqueous alcohol in brown crystals and melts at 73—74°.

2:4-Dinitrodiphenylamine, obtained by warming aniline with chloro-2:4-dinitrobenzene, is found to melt at 155—156° (compare

Clemm, *J. pr. Chem.*, 1870, [ii], 1, 145; Willgerodt, Abstr., 1876, 405; Hepp, Abstr., 1879, 50).

2 : 4-Dinitrophenyl-*p*-toluidine crystallises in red needles, melts at 131°, and is easily soluble in ether forming a yellow solution (Engelhardt and Latschinoff, this Journ., 1871, 1053; Willgerodt, *loc. cit.*). 2 : 4-*Dinitrophenylethyl*-p-*toluidine*, $C_6H_3(NO_2)_2\cdot NEt\cdot C_7H_7$, separates from aqueous alcohol in yellow crystals and melts at 120°.

2 : 4-*Dinitrophenyl*-m-*toluidine* crystallises in red needles and melts at 159°.

2 : 4-Dinitrophenyl-*o*-toluidine forms yellow crystals and melts at 120° (Leymann, *Diss. Berlin*, 1881). 2 : 4-*Dinitrophenylmethyl*-o-*toluidine* forms orange-coloured crystals and melts at 155°. 2 : 4-*Dinitrophenylethyl*-o-*toluidine* separates from alcohol in canary-yellow crystals and melts at 114°.

Dinitrophenylpyridine chloride is found to melt at 201°, and its platinichloride at 220° (Gail, *Diss. Marburg*, 1899; Spiegel, Abstr., 1900, i, 51). The action of dinitrophenylpyridine chloride on benzidine leads to the formation of a *hydrochloride*, $C_{29}H_{27}N_4Cl$, which has a moss-green colour, melts at 179—180°, and dissolves in methyl alcohol to a deep red solution.

The action of chlorodinitrobenzene on benzidine and pyridine in alcoholic solution leads to the formation of benzidine hydrochloride and 2 : 4-dinitrophenylbenzidine.

Formanilide and dinitrophenylpyridine chloride yields a rose-coloured *substance*, $C_{19}H_{17}O_2N_2Cl$ (?), which melts at 193°. G. Y.

[2 : 4-Dinitro-4′-hydroxydiphenylamine-2′-sulphonic Acid.] Kalle & Co. (D.R.-P. 143494).—1-Chloro-2-dinitrobenzene condenses with 4-aminophenol-3-sulphonic acid in alkaline solution, forming 2 : 4-*dinitro-4′-hydroxydiphenylamine-2′-sulphonic acid*, which crystallises from benzene in brown leaflets. When fused with sodium sulphide and sulphur at 120°, a black dye is formed, dissolving in water to a greenish-blue solution, and precipitated by hydrochloric acid as a brown solid. C. H. D.

Relations between the Colour, Composition, and Constitution of the Alkali Derivatives of the Nitrophenols. Joseph C. W. Frazer (*Amer. Chem. J.*, 1903, **30**, 309—323).—The variation in the colour of the sodium and potassium derivatives of *o*- and *p*-nitrophenol has been studied by Carnelly and Alexander (Proc., 1888, **4**, 64).

In the present paper, an account is given of the sodium, potassium, rubidium, and cæsium derivatives of the three nitrophenols and 1 : 2 : 3-nitrocresol. *Rubidium* o-*nitrophenoxide* crystallises from water in orange-yellow plates containing $\frac{1}{2}H_2O$; when crystallised from alcohol, the anhydrous salt is obtained in red needles. *Cæsium* o-*nitrophenoxide* forms scarlet crystals which contain no water of crystallisation. *Sodium* m-*nitrophenoxide* crystallises in small, orange-red needles containing $1H_2O$. *Rubidium* m-*nitrophenoxide* forms small, yellow needles; the *compound*,

$$NO_2\cdot C_6H_4\cdot ORb,NO_2\cdot C_6H_4\cdot OH,$$

crystallises in brownish-red, radiating needles. *Cæsium* m-*nitro*

phenoxide forms the *compound*, $NO_2 \cdot C_6H_4 \cdot OCs, NO_2 \cdot C_6H_4 \cdot OH$, which is obtained in brilliant, almost blood-red crystals. Sodium *p*-nitrophenoxide crystallises with $4H_2O$, but after exposure to the air for some time the crystals contain only $2H_2O$. Potassium *p*-nitrophenoxide is found to crystallise with $1H_2O$, whereas, according to Post and Mehrtens (Abstr., 1876, i, 579), the crystals contain $2H_2O$. *Rubidium* p-*nitrophenoxide* crystallises in yellow needles containing $1H_2O$; the *cæsium* derivative forms yellow plates with $3H_2O$. *Sodium* 1 : 2 : 3-*nitrotolyloxide* forms light red needles containing $2H_2O$; the *potassium* derivative crystallises in light red scales with $\frac{1}{2}H_2O$; the *rubidium* derivative forms dark cherry-red, monoclinic crystals containing $1H_2O$; the *cæsium* derivative is of a red colour, but could not be obtained in a pure state.

The electric conductivities of *o*-, *m*-, and *p*-nitrophenols were determined at different dilutions. The results show that *m*- and *p*-nitrophenols are dissociated to about the same extent, whilst both are dissociated somewhat more than *o*-nitrophenol.

The absorption spectra of some of the metallic derivatives of *o*- and *p*-nitrophenols were examined. It was observed that with solutions of *p*-nitrophenoxide the light is not absorbed so far in the direction of the red end of the spectrum as is the case with solutions of *o*-nitrophenoxides of corresponding strength.

With regard to the colour of the three classes of nitrophenoxides, the *o*-nitrophenoxides possess a colour that is nearest the red end of the chromatic scale, that of the *p*-nitrophenoxides is furthest from the red end, whilst that of the *m*-nitrophenoxides occupies an intermediate position. In each series of nitrophenoxides, the colour becomes lighter as the atomic weight of the metal increases, but this is less noticeable in the para- than in the ortho- and meta-series. The change of colour due to water of crystallisation is greatest in the case of the *o*-nitrophenoxides and least in the para-compounds. The anhydrous *o*-nitrophenoxides are red, the anhydrous meta-compounds are of a lighter red colour, whilst the anhydrous para-compounds are yellow, with the exception of the sodium derivative, which is red.

The nitrotolyloxides are all red, but not so dark as the *o*-nitrophenoxides; their variation in colour among one another is less than in the case of the *o*- and *m*-nitrophenoxides. The change of colour due to water of crystallisation is less than in the case of the *o*- and *m*-nitrophenoxides. E. G.

Preparation of 3-Chloro-4-aminophenol. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 143449).—Fused *m*-chlorophenol is added to nitric acid, the temperature being maintained below 15°. The product is almost exclusively 3-*chloro*-4-*nitrophenol*, which crystallises from benzene in small needles and melts at 133°. Iron and hydrochloric acid reduce it to 3-*chloro*-4-*aminophenol*, this compound separating in white needles melting at 160°. C. H. D.

[Substituted Phenyl Benzyl Ethers.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 142061 and 142899).—The following compounds are described :

	M. p.
o-*Nitrophenyl* o-*chlorobenzyl ether*	89°
2-*Nitro-4-tolyl* o-*chlorobenzyl ether*	104
4-*Chloro-2-nitrophenyl* o-*chlorobenzyl ether*	117
o-*Nitrophenyl* p-*chlorobenzyl ether*	75—78
2-*Nitro-4-tolyl* p-*chlorobenzyl ether*	103
o-*Aminophenyl* o-*chlorobenzyl ether hydrochloride*	191
2-*Amino-4-tolyl* o-*chlorobenzyl ether hydrochloride*	208
4-*Chloro-2-aminophenyl* o-*chlorobenzyl ether hydrochloride*	189
o-*Aminophenyl* p-*chlorobenzyl ether hydrochloride*	194—197
2-*Amino-4-tolyl* p-*chlorobenzyl ether hydrochloride*	195—200

The hydrochlorides are soluble in alcohol, and decompose on heating with water, the bases form colourless crystals, insoluble in cold water.

	M. p.
4-*Chloro-2-nitrophenyl benzyl ether*	86°
4-*Chloro-2-aminophenyl benzyl ether hydrochloride*	168—173
4-*Bromo-2-nitrophenyl benzyl ether*	88—90
4-*Bromo-2-aminophenyl benzyl ether hydrochloride*	187
4-*Bromo-2-nitro-5-tolyl benzyl ether*	oily
4-*Bromo-2-amino-5-tolyl benzyl ether hydrochloride*	245—250

The amino-compounds, when diazotised, combine with β-naphthol to form fast red dyes. C. H. D.

Action of Phosphorus on Carbon Compounds. I. HERMANN WICHELHAUS (*Ber.*, 1903, **36**, 2942—2944).—Dinaphthyl oxide is the chief product formed when β-naphthol is heated with red phosphorus in an atmosphere of carbon dioxide at about 200° under atmospheric pressure. Hydrogen phosphide and phosphorous acid are also formed, probably according to the equation $2P + 6C_{10}H_8O = H_3PO_3 + PH_3 + 3C_{20}H_{14}O$. Even under slightly increased pressures, the products are practically the same, but if the reaction is conducted in sealed tubes, so that the hydrogen phosphide cannot escape, the chief product is naphthalene. It is suggested that the method may be of use in determining the constitution of compounds containing oxygen.

α-Naphthol and phosphorus yield naphthalene and also dinaphthylene oxide.

Phenol also reacts with red phosphorus, yielding hydrogen phosphide and condensation products.

In sealed tubes, phosphorus reacts more energetically on phenol, and an oil boiling at 193—194° and containing this element is formed.

J. J. S.

Condensation in presence of Metals and their Chlorides. MARUSSIA BAKUNIN (*Gazzetta*, 1903, **33**, i, 495—496).—In order to prevent the formation of resinous products due to the high temperatures often attained in condensation reactions brought about by metals or metallic chlorides, the author suggests that such reactions should be carried out in presence of neutral solvents. By this means, the substances employed are in a finer state of division, and, further, by suitable choice of solvent, the best temperature for any particular condensation may be obtained.

Working in this way, the author has carried out condensations of phenols with benzyl chloride in presence of zinc, and has obtained the hitherto unknown benzyl derivatives of α- and β-naphthols in a pure crystalline form. Instead of separating the products by distillation, it is better to employ treatment with sodium hydroxide, in which these benzyl derivatives are usually soluble and the other products insoluble. T. H. P.

β-Phenylethyl Alcohol. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1903, [iii], **30**, 953—954. Compare Abstr., 1902, i, 198).—When trioxymethylene, dissolved in ether, is treated with magnesium benzyl chloride and the mixture heated at 100° for two days, a yield of 35 per cent. of β-phenylethyl alcohol is obtained, together with some dibenzyl. The alcohol crystallises in long needles, melts at 33°, and has a sp. gr. 1·0389 at 15·2°/0°. The *acetate* is a mobile liquid and boils at 228—230° under 753 mm. pressure. T. A. H.

Degradation of Cholesterol. OTTO DIELS and EMIL ABDERHALDEN (*Ber.*, 1903, **36**, 3177—3182).—When oxidised with sodium hypobromite, cholesterol yields, among other products, an *acid*, $C_{20}H_{32}O_3$, which crystallises from methyl ethyl ketone in measurable crystals belonging to the tetragonal-holohedric system. It sinters at 282°, melts at 297° (corr.), and is sparingly soluble in most organic solvents and in water, but easily soluble in alkali hydroxides. The *silver* salt, $C_{40}H_{61}O_6Ag_3$, crystallises in needles; hydrogen sulphide reconverts it into the acid. The *ethyl ester*, $C_{22}H_{36}O_3$, crystallises from methyl alcohol in brilliant, hexagonal plates, sinters at 143°, melts at 149°, and yields the original acid on hydrolysis with alkali hydroxides. E. F. A.

Behaviour of Benzhydrol when heated alone and in presence of Spongy Palladium. EMIL KNOEVENAGEL and W. HECKEL (*Ber.*, 1903, **36**, 2816—2822).—Benzhydrol, when heated in a stream of carbon dioxide, is decomposed into hydrogen and benzophenone. The amount of hydrogen liberated from 2 grams in 2 hours was 30 c.c. at 280—285°, 38 c.c. at 285—290°, 45 c.c. at 290—295°, and 60 c.c. at 290°; the theoretical quantity being 242 c.c. and the maximum amount of decomposition about 25 per cent. The decomposition is facilitated by the presence of palladium, the gas liberated in 2 hours from 2 grams of benzhydrol with 0·5 gram of palladium being 25 c.c. at 200—210°, 31 c.c. at 215—220°, 33 c.c. at 230—235°, 42 c.c. at 255—260°, 62 c.c. at 270—275°, and 75 c.c. at 285—290°. Under these conditions, much of the hydrogen is retained by the palladium, especially at the lower temperatures; in presence of 0·1 gram of palladium at 295°, the gas liberated from 2 grams of benzhydrol in one hour amounted in three experiments to 165, 182, and 175 c.c. Experiments at constant temperature showed that the change proceeded as a unimolecular reaction, the action being especially regular when the benzhydrol was diluted with several times its weight of benzophenone. T. M. L.

Behaviour of Benzhydrol when heated in presence of Copper Powder. EMIL KNOEVENAGEL and W. HECKEL (*Ber.*, 1903, **36**, 2823—2829).—In presence of copper powder, the decomposition of benzhydrol by heat yields benzhydrol ether, tetraphenylethane, and diphenylmethane, the decomposition into benzophenone and hydrogen being much less than when heated alone or with palladium. Thus in presence of 0·5 gram of copper powder, 2 grams of benzhydrol yielded in 2 hours only 10 c.c. of hydrogen at 210° and at 230°, 12 c.c. at 250°, 9 c.c. at 270°, and 6 c.c. at 290°, but the weight of benzhydrol ether was 0·6 gram at 210°, decreasing to 0·1 gram at 290°, whilst the tetraphenylethane increased from a trace at 210° to 0·6 gram at 290°; in presence of only 0·2 gram of copper, there was a very much greater formation of benzophenone and hydrogen at all temperatures above 230°; an increase in the weight of copper powder to 50 or 100 per cent. did not materially reduce the amount of benzophenone and hydrogen produced, but gave an improved yield of benzhydrol ether at 210° and a steady yield of 30 per cent. of tetraphenylethane at 290°. A 70 per cent. yield of benzhydrol ether can be obtained by heating benzhydrol in the absence of air at 210—220° with half its weight of copper powder.

The tendency of palladium to cause the separation of hydrogen whilst copper causes the separation of water is a good example of the way in which the course of a decomposition may be varied by altering the catalytic agent. T. M. L.

Tribenzylcarbinol. FRANZ SACHS and HERMANN LOEVY (*Ber.*, 1903, **36**, 3236).—The substance described as tribenzylcarbinol (this vol., i, 592) is really impure dibenzyl; the real *tribenzylcarbinol*, prepared from magnesium benzyl bromide and ethyl phenylacetate, crystallises from dilute alcohol and melts at 114°. Tritolylcarbinol (*loc. cit.*) was also probably impure. W. A. D.

***p*-Hydroxytriphenylcarbinol and its Derivatives.** KARL AUWERS and O. SCHRÖTER (*Ber.*, 1903, **36**, 3236—3254).—The substance formerly described as 3 : 5-dibromo-4-hydroxytriphenylcarbinol (Bistrzycki and Herbst, Abstr., 1901, i, 701) is really the anhydride, 4-*diphenylmethylene*-2 : 6-*dibromoquinone*, $CPh_2{:}C_6H_2Br_2{:}O$; it is best prepared by brominating *p*-hydroxytriphenylcarbinol and melts at 232°, not at 225°. On acetylation, it gives 3 : 5-*dibromo*-4-*acetoxytriphenylcarbinol*, $OH{\cdot}CPh_2{\cdot}C_6H_2Br_2{\cdot}OAc$, melting at 171—172°, which was considered by Bistrzycki and Herbst to be dibromo-*p*-acetoxytriphenylmethyl ether. 3 : 5-*Dibromo*-4-*hydroxytriphenylcarbinol*, $OH{\cdot}CPh_2{\cdot}C_6H_2Br_2{\cdot}OH$, prepared by the addition of water to the diphenylmethylenequinone dissolved in aqueous acetone, crystallises from light petroleum containing benzene in lustrous, colourless, thick prisms or plates, melts at 138°, and is reconverted into the quinone by warm acetic acid.

3 : 5-*Dibromo*-4-*hydroxytriphenylmethyl bromide*,

$$CPh_2Br{\cdot}C_6H_2Br_2{\cdot}OH,$$

obtained by the addition of hydrogen bromide to the quinone, is rather unstable, being resolved into its constituents when exposed to

moist air; it forms flat, lustrous needles and melts indefinitely between 130° and 140°. It easily regenerates the quinone when water is added to its solution in acetone, and instead of interacting with sodium acetate or organic bases as a pseudo-phenol, it merely loses hydrogen bromide; with acetic anhydride in the same way, it gives a mixture of the methylenequinone and 3:5-dibromo-4-acetoxytriphenylcarbinol.

Analyses of Bistrzycki and Herbst's *p*-hydroxytriphenylcarbinol, recrystallised from dilute acetic acid and melting at about 140°, show that it is apparently a hydrate, $C_{19}H_{16}O_2,\frac{1}{2}H_2O$. The anhydrous substance is obtained by dissolving the hydrate in alkali, precipitating with carbon dioxide, and crystallising the product from benzene; it melts at about 165°. Whilst the pure anhydrous substance is stable at 100°, the hydrate or the anhydrous form containing traces of water is converted into a bright yellow substance insoluble in alkalis; this is not an ether, $O(CPh_2{\cdot}C_6H_4{\cdot}OH)_2$, as supposed by Bistrzycki and Herbst, because determinations of its molecular weight in various solvents gave values lying between 241 and 280, and the formula quoted requires a molecular weight 534; the nature of the substance is still uncertain.

Diphenylmethylenequinone is most easily prepared by heating *p*-hydroxytriphenylcarbinol for 2 hours at 200° (compare *loc. cit.*).

W. A. D.

Action of Carbon Dioxide on Magnesium Phenyl Bromide. Georg Schroeter (*Ber.*, 1903, 36, 3005—3007).—By the action of carbon dioxide on magnesium phenyl bromide, there are produced not only benzoic acid, but benzophenone, triphenylcarbinol, diphenyl (probably produced directly from the magnesium and bromobenzene), and a *compound* which melted at 165°, but did not again solidify and had been rendered soluble in alcohol; this is perhaps an unstable molecular compound of benzophenone and triphenylcarbinol, $CPh_3{\cdot}O{\cdot}CPh_2{\cdot}OH$.

T. M. L.

Action of Silver Cyanate on Acyl Chlorides. II. Benzoylcarbimide. Otto C. Billeter (*Ber.*, 1903, 36, 3218—3221. Compare this vol., i, 484).—Benzoylcarbimide, $C_6H_5{\cdot}CO{\cdot}N{:}CO$, crystallises from ether, cooled in ice, in very large, colourless prisms melting at 25·5—26°, and decomposing rapidly in moist air. When fused, it is a colourless liquid with faint disagreeable odour, miscible in all proportions with ether or benzene, and boiling at 88° under 10 mm., at 202·5—204° under 724 mm. pressure. Water decomposes it violently into benzamide and dibenzoylcarbamide. Alcohol forms benzoylurethane and aniline forms benzoylphenylcarbamide. Dry ammonia reacts in ethereal solution forming benzoylcarbamide. Benzenesulphonamide forms *benzoylbenzenesulphonylcarbamide*, $C_{14}H_{12}O_4N_2S$, crystallising from glacial acetic acid in felted, silky needles melting at 208°. Ethylene glycol yields *hydroxyethyl benzoylcarbamate*, $NHBz{\cdot}CO_2{\cdot}C_2H_4{\cdot}OH$, which forms colourless crystals melting at 148°. C. H. D.

Ethyl *o*-Hydroxylaminobenzoate. EUGEN BAMBERGER and F. PYMAN (*Ber.*, 1903, 36, 2700—2701. Compare Alway and Walker, this vol., i, 696).—*Ethyl* o-*hydroxylaminobenzoate*, $CO_2Et{\cdot}C_6H_4{\cdot}NH{\cdot}OH$, prepared by reducing ethyl *o*-nitrobenzoate with zinc dust and ammonium chloride, crystallises in white, silky needles, softens at 76°, and melts at 78·5°. It differs from other arylhydroxylamines in being almost insoluble in dilute acids and in not reducing Fehling's solution; it dissolves in dilute aqueous sodium hydroxide and seems to be decomposed, as, on adding acid, a *substance* crystallising in needles and melting at 111° is obtained. Oxidising agents readily convert the ester into ethyl *o*-nitrosobenzoate. W. A. D.

Isomeric Chlorides of *o*-Sulphobenzoic Acid. IRA REMSEN (*Amer. Chem. J.*, 1903, 30, 247—309. Compare Abstr., 1895, i, 243, 244, and 1897, i, 472, 473).—It has been shown by List and Stein (Abstr., 1898, i, 584) that the substance described by the author as the unsymmetrical chloride of *o*-sulphobenzoic acid, melting at 21—22°, is a mixture of the chloride, melting at 79°, with another which melts at 40°. The chloride of low melting point used in the experiments described in the present paper is the compound melting at 40°, prepared by List and Stein's method. It is considered probable that the chloride of higher melting point has the constitution

$$COCl{\cdot}C_6H_4{\cdot}SO_2Cl,$$

whilst the other has the constitution $C_6H_4{<}{}^{CCl_2}_{SO_2}{>}O$, and these compounds are termed the symmetrical and unsymmetrical chlorides respectively.

[With R. M. BIRD.]—The action of ammonia on the two chlorides has been reinvestigated and the previous results confirmed. The symmetrical chloride yields only the ammonium salt of benzoicsulphinide, whilst the unsymmetrical compound furnishes ammonium *o*-cyanobenzenesulphonate together with a varying quantity of the ammonium salt of benzoicsulphinide.

When the unsymmetrical chloride is treated with dilute aqueous ammonia, the reaction takes place very slowly and only a trace of the sulphinide is produced. With a stronger solution of ammonia, the amount of sulphinide produced forms 4—20 per cent. of the total product. If, however, the chloride is dissolved in dry ether or chloroform and dry ammonia is passed into the solution, ammonium *o*-cyanobenzenesulphonate only is obtained. The action of ammonia on the symmetrical chloride is much slower than on the unsymmetrical compound, and yields the ammonium salt of benzoicsulphinide and ammonium chloride.

It has been shown previously that the symmetrical chloride reacts with alcohols with formation of acid esters, $CO_2R{\cdot}C_6H_4{\cdot}SO_3H$, whereas the unsymmetrical chloride yields, in the first place, ester chlorides, $CO_2R{\cdot}C_6H_4{\cdot}SO_2Cl$, which, in turn, give the acid esters. When, however, an ethereal solution of the symmetrical chloride is treated with sodium ethoxide, the ester chloride is apparently produced. Sodium ethyl *o*-sulphobenzoate crystallises in plates or hexagonal

prisms. The *silver*, *barium*, and *sodium* sulphonates of methyl benzoate, and the *disodium* salt of *o*-sulphobenzoic acid, $CO_2Na\cdot C_6H_4\cdot SO_3Na$, are described.

[With Willis B. Holmes.]—The earlier investigations on the action of aniline on the chlorides of *o*-sulphobenzoic acid have shown that the symmetrical chloride yields the symmetrical anilide only. List and Stein (*loc. cit.*), however, have stated that each of the chlorides furnishes a mixture of the two anilides and the anil.

It is now found that when the symmetrical chloride is treated with aniline in presence of water, the only products are the symmetrical anilide and the anil, whilst the unsymmetrical chloride, when treated in the same way, yields a mixture of the two anilides but no anil; if, however, aniline is added to an ethereal solution of either chloride, all three products are formed.

[With Friend E. Clark.]—The symmetrical chloride of *o*-sulphobenzoic acid reacts with primary amines with formation of esters of benzoicsulphinide, $C_6H_4<{CO \atop SO_2}>NR$, whilst the unsymmetrical chloride yields small quantities of the esters of benzoicsulphinide together with infusible disubstituted amides, $C_6H_4<{C(NHR)_2 \atop SO_2}>O$. The symmetrical chloride reacts with secondary amines with production of compounds of the general formula $NR_2\cdot CO\cdot C_6H_4\cdot SO_2\cdot NR_2$.

Methylbenzoicsulphinide, first prepared by Remsen and Palmer (Abstr., 1887, 144), crystallises from alcohol in slender needles, melts at 129°, and is slightly soluble in hot water. When boiled with hydrochloric acid, it undergoes hydrolysis with formation of the *methylamine* salt of *o*-sulphobenzoic acid, $CO_2H\cdot C_6H_4\cdot SO_3H,NH_2Me$. By the action of alcoholic potassium hydroxide on methylbenzoicsulphinide, *potassium o-methylsulphaminebenzoate*, $CO_2K\cdot C_6H_4\cdot SO_2\cdot NMeK$, is produced; the corresponding *barium* salt was prepared and analysed.

o-*Toluenesulphonic methylamide*, $C_6H_4Me\cdot SO_2\cdot NHMe$, obtained by the action of methylamine on *o*-toluenesulphonic chloride, crystallises from acetone in thin, striated plates, melts at 73—75°, and is soluble in alcohol or chloroform. On oxidation with alkaline permanganate, it yields potassium *o*-methylsulphaminebenzoate; when this salt is treated with hydrochloric acid at the ordinary temperature, it is converted into methylbenzoicsulphinide, but if the temperature is lowered to 10° before the addition of the acid, o-*methylsulphaminebenzoic acid* is produced, which crystallises in small, radiating needles, softens at 70°, and is completely melted at 126°.

By the action of aqueous methylamine on the symmetrical chloride, methylbenzoicsulphinide is produced together with a small quantity of the symmetrical dimethylamide of *o*-sulphobenzoic acid.

When dry methylamine is passed into an ethereal solution of the unsymmetrical chloride, a small quantity of methylbenzoicsulphinide is obtained together with the unsymmetrical *dimethylamide* of *o*-sulphobenzoic acid, $C_6H_4<{C(NMe_2)_2 \atop SO_2}>O$, which crystallises from alcohol in plates and does not melt below 330°.

When an ethereal solution of the symmetrical chloride is treated with dry ethylamine, ethylbenzoicsulphinide is produced. This compound is hydrolysed by alcoholic alkali hydroxide with the formation of *potassium o-ethylsulphaminebenzoate*, $CO_2K\cdot C_6H_4\cdot SO_2\cdot NEtK$; the corresponding *barium* salt was prepared. The *ethylamine* salt, $CO_2H\cdot C_6H_4\cdot SO_2H,NH_2Et$, crystallises in needles.

By the action of ethylamine on the unsymmetrical chloride, ethylbenzoicsulphinide is produced together with the infusible unsymmetrical *diethylamide*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{C(NEt)_2}{SO_2}}{>}O$, which crystallises in rhombic prisms, is soluble in alcohol, and sparingly so in benzene or acetone.

When an ethereal solution of either the symmetrical or unsymmetrical chloride is treated with dimethylamine, the symmetrical *tetramethyldiamide*, $NMe_2\cdot CO\cdot C_6H_4\cdot SO_2\cdot NMe_2$, is obtained, which crystallises in rhombic prisms [$a:b:c = 0{\cdot}232:1:0{\cdot}127$]; this compound is hydrolysed by concentrated aqueous alkali hydroxide with formation of *o*-sulphobenzoic acid and dimethylamine, but is unaffected by alcoholic alkali hydroxides.

[With Robert E. Humphreys.]—It has been stated by Remsen and McKee (Abstr., 1897, i, 244) that when the symmetrical chloride of *o*-sulphobenzoic acid is treated with phenol, the diphenyl ester, $CO_2Ph\cdot C_6H_4\cdot SO_3Ph$, and the phenyl ester chloride, $CO_2Ph\cdot C_6H_4\cdot SO_2Cl$, are formed. The latter compound was not isolated, but was identified by its conversion into phenyl *o*-sulphaminebenzoate by the action of ammonia; List and Stein (*loc. cit.*), however, were unable to find any evidence of the production of this substance.

The work of Remsen and McKee has now been repeated and their results confirmed. It is found, however, that the sulphochloride, $CO_2Ph\cdot C_6H_4\cdot SO_2Cl$, does not react with ammonia directly, but that when a mixture of the symmetrical chloride and phenol is treated with ammonia, phenyl *o*-sulphaminebenzoate is produced. When the symmetrical chloride is heated with phenol at 40—45°, diphenyl *o*-sulphobenzoate and the *o*-sulphochloride of phenyl benzoate are obtained. If the unsymmetrical chloride is treated with phenol and ammonia, diphenyl *o*-sulphobenzoate and ammonium *o*-cyanobenzenesulphonate are produced, but no phenyl *o*-sulphaminebenzoate is formed.

The action of *o*- and *p*-cresols on the chlorides of *o*-sulphobenzoic acid was examined. It was found that they react less readily than phenol with the symmetrical chloride, and do not react at all with the unsymmetrical compound. o-*Tolyl o-sulphaminebenzoate* melts at 152°. The p-*tolyl* ester was also prepared.

Phenyl *o*-carbaminesulphonate, $NH_2\cdot CO\cdot C_6H_4\cdot SO_3Ph$, crystallises in plates or needles and melts at 95°.

Attempts were made to prepare phenyl *o*-sulphaminebenzoate directly from the acid itself, but without success.

Experiments were carried out with the object of determining the relative proportions of the *o*-sulphochloride of phenyl benzoate and diphenyl *o*-sulphobenzoate formed by the action of phenol on the chlorides of *o*-sulphobenzoic acid; the results showed that the best yield of the *o*-sulphochloride of phenyl benzoate is obtained when the

unsymmetrical chloride (1 mol.) is heated with phenol (2 mols.) at 40—45° for 12—16 hours. The *o*-sulphochloride of phenyl benzoate forms large, colourless crystals, melts at 103—104°, and is readily soluble in alcohol or glacial acetic acid. It is easily hydrolysed by hydrochloric or sulphuric acid with formation of *o*-sulphobenzoic acid. When it is heated with a solution of barium hydroxide, the barium salt and diphenyl ester of *o*-sulphobenzoic acid are produced; a similar change is brought about by the action of potassium hydroxide, whilst by that of ammonia the ammonium salt of benzoicsulphinide is obtained. When the *o*-sulphochloride of phenyl benzoate is treated with aniline, *o*-sulphobenzanil (Remsen and Coates, Abstr., 1895, 473) is produced.

By the action of dilute potassium hydroxide on a mixture of the symmetrical chloride and phenol, diphenyl *o*-sulphobenzoate only is produced, whilst the unsymmetrical chloride, under these conditions, yields the diphenyl ester together with the *o*-sulphochloride of phenyl benzoate.

When the unsymmetrical chloride is heated with *o*-cresol, the o-*sulphochloride* of *o*-tolyl benzoate, $SO_2Cl\cdot C_6H_4\cdot CO_2\cdot C_7H_7$, is obtained, which forms rhombic crystals and melts at 112°. No definite product could be isolated when the symmetrical chloride was treated in the same way.

When treated with *o*-cresol and dilute potassium hydroxide, the unsymmetrical chloride yields the *o*-sulphochloride of *o*-tolyl benzoate, whilst the symmetrical chloride is decomposed, a small quantity of *di-o-tolyl o-sulphobenzoate* being formed, which crystallises in needles and melts at 141°.

When the unsymmetrical chloride is heated with *p*-cresol, or treated with *p*-cresol and dilute potassium hydroxide, the *o*-sulphochloride of *p*-tolyl benzoate is produced, and, in either case, if the temperature is high, some di-*p*-tolyl *o*-sulphobenzoate is also formed. The symmetrical chloride, when similarly treated, is converted into di-*p*-tolyl *o*-sulphobenzoate. E. G.

Comparative Study of *m*-Sulphaminebenzoic Acids made by Different Methods. JOSEPH C. W. FRAZER (*Amer. Chem. J.*, 1903, 30, 323—330).—It is found that *m*-sulphaminebenzoic acid, whether prepared from *m*-sulphobenzoic diamide, from the *m*-sulphochloride of benzoic acid, from *m*-sulphaminebenzonitrile, from *p*-bromo-*m*-toluenesulphonic acid, or from *p*-amino-*m*-toluenesulphonic acid, is one and the same substance. When heated rapidly, it melts at 237—238° (corr.), but when heated slowly it undergoes a change that causes it to melt as low as 215°. E. G.

Action of Ethyl Chlorocarbonate on Magnesium Alkyl Haloids. JOSEPH HOUBEN (*Ber.*, 1903, 36, 3087—3089).—Ethyl benzoate may be synthesised by the addition of an ethereal solution of magnesium phenyl bromide to an ethereal solution of ethyl chlorocarbonate. If the ethyl chlorocarbonate is added to the solution of the magnesium compound, the chief product is triphenylcarbinol

(34 per cent.), and only a small amount (16·6 per cent.) of ethyl benzoate is obtained.

Ethyl phenylacetate and tribenzylcarbinol (Sachs and Loevy, this vol., i, 592) have been obtained by similar methods from magnesium benzyl chloride and ethyl chlorocarbonate. Tribenzylcarbinol melts at 108—111°, whereas Sachs and Loevy give the melting point as 55°. Ethyl bromoacetate cannot be substituted for ethyl chlorocarbonate. J. J. S.

Blue Dyes of the Diphenylnaphthylmethane Series. DAVID MARON (D.R.-P. 144536).—α-Naphthylaminobenzyl cyanide,

$$C_{10}H_7\cdot NH\cdot CHPh\cdot CN$$

(Sachs and Goldmann, Abstr., 1902, i, 780), condenses with tetramethyldiaminobenzophenone in presence of phosphorus oxychloride, forming a crystalline blue dye, dissolving in alcohol or acetic acid to a dark blue solution. The solution in concentrated sulphuric acid is reddish-brown, becoming dark green on dilution.

Aldehyde cyanohydrin combines with α-naphthylamine when heated in a closed vessel on the water-bath to form *α-naphthylaminoethyl cyanide*, $C_{10}H_7\cdot NH\cdot CHMe\cdot CN$, crystallising from alcohol in prisms melting at 104—105°. It forms a condensation product similar to the foregoing dye. C. H. D.

Attempts to prepare Tetrahydroxyindigotin. F. HAYDUCK (*Ber.*, 1902, 36, 2930—2936).—*Dibenzoylprotocatechuic aldehyde*, $C_6H_3(OBz)_2\cdot CHO$, obtained by the Schotten-Baumann method, crystallises from alcohol in colourless needles melting at 98°, and yields a *phenylhydrazone* crystallising in yellow plates and melting at 167°. When nitrated, it yields a *dinitro*-derivative,

$$C_6H_3(O\cdot CO\cdot C_6H_4\cdot NO_2)_2\cdot COH,$$

crystallising from alcohol in indefinite, colourless nodules.

o-*Nitroprotocatechuic aldehyde*, $[CHO : NO_2 : (OH)_2 = 1 : 2 : 4 : 5]$, obtained by passing nitrous gases into a solution of protocatechuic aldehyde in ether, crystallises from a mixture of ether and light petroleum in yellow needles melting at 176° It yields a *dimethyl ether* in the form of colourless needles melting at 63°. The addition of a few drops of potassium hydroxide solution to an aqueous acetone solution of the dimethyl ether produced bluish-violet needles of *tetramethoxyindigotin*, $C_6H_2(OMe)_2{<}^{NH}_{CO}{>}C{:}C{<}^{NH}_{CO}{>}C_6H_2(OMe)_2$, which is somewhat more soluble in alcohol or acetone than ordinary indigotin. In a vacuum, it sublimes above 300° in the form of dark violet needles with an intense metallic lustre. It does not yield dyes with the common mordants. So far it has not been found possible to obtain tetrahydroxyindigotin from the methoxy-derivative.

Nitrovanillin, $OH\cdot C_6H_2(OMe)(NO_2)\cdot CHO$, obtained by the action of nitrous fumes on an ethereal solution of vanillin, crystallises in yellow needles or plates melting at 175—176°. Its *potassium* derivative crystallises from water in orange-coloured needles containing water of crystallisation, which it loses at 130°. When the nitro-compound is heated at 140° with concentrated hydrochloric acid, it

yields a *nitroprotocatechuic aldehyde*, $[CHO:NO_2:(OH)_2 = 1:3:4:5]$, in the form of yellow needles melting at 106°. Its *potassium* salt forms a purplish-black precipitate.

Bisdioxymethyleneindigotin (Abstr., 1890, 1140) yields with phosphorus oxychloride *tetrachlorobisdioxymethyleneindigotin* in the form of a blackish-green precipitate, but this, so far, has not been transformed into tetrahydroxyindigotin.

Caffeic acid has been obtained by warming protocatechuic aldehyde, acetic acid, and malonic acid on the water-bath, but it has not been found possible to nitrate it by the method described above.

Dibenzoylprotocatechuic aldehyde condenses with malonic acid in the presence of acetic acid yielding the *dibenzoyloxybenzylidenemalonic acid*, $C_6H_3(OBz)_2{\cdot}CH{:}C(CO_2H)_2$, which melts and decomposes at 200—201°. It is converted by loss of carbon dioxide into *dibenzoylcaffeic acid*, which crystallises in colourless needles melting at 204—206°. The *ethyl* ester, $C_6H_3(OBz)_2{\cdot}CH{:}CH{\cdot}CO_2Et$, crystallises in long, colourless needles melting at 104—105°. J. J. S.

Benzoylation of Isatin, Indigotin, and Anthranil. Gustav Heller (*Ber.*, 1903, 36, 2762—2766).—From a study of benzoylanthranil, the author has been led to assign the formula I to anthranil:

$$\text{I.}\quad C_6H_4<\begin{matrix}CO\\|\\NH\end{matrix} \qquad\qquad \text{II.}\quad C_6H_4<\begin{matrix}CH\\|\\N-\end{matrix}>O.$$

Bamberger (this vol., i, 432) opposes this formula, adopting the formula II, and rejects the evidence derived from the benzoyl derivative on the ground that the benzoylation of anthranil only takes place at a high temperature. It is now shown that isatin, $C_6H_4<\begin{matrix}CO-\\NH\end{matrix}>CO$, and indigotin, $C_6H_4<\begin{matrix}CO-\\NH\end{matrix}>C{:}C<\begin{matrix}CO-\\NH\end{matrix}>C_6H_4$, closely resemble anthranil in this respect.

Isatin is only converted to a small extent into benzoyl-ψ-isatin by heating with benzoyl chloride at 170°. Indigotin reacts with benzoyl chloride in pyridine solution at 100°, yielding *tetrabenzoylindigo-white*, $C_{44}H_{28}O_6N_2$, which forms colourless needles melting at 217—218°, and dissolving readily in benzene or pyridine, less readily in ether. Aqueous sodium hydroxide has very little action, alcoholic sodium hydroxide hydrolyses it readily, hydrochloric acid is without action. The solution in concentrated sulphuric acid becomes greenish-blue on heating. Unlike Vorländer and Drescher's dibenzoylindigo-white (Abstr., 1901, i, 563), the compound is not oxidised by sodium nitrite or potassium dichromate. The benzoylation of anthranil is quantitative at 145—150°; in pyridine solution, a 75 per cent. yield is obtainable on the water-bath. C. H. D.

Synthesis of β-Hydroxy-β-anisylpivalic Acid [β-Hydroxy-β-p-anisyl-αα-dimethylpropionic Acid]. L. Baidakowsky (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 488—498).—*Ethyl β-hydroxy-β-*p*-anisyl-αα-dimethylpropionate*, $C_{14}H_{20}O_4$, prepared by the condensation of molecular proportions of anisaldehyde and ethyl bromo*iso*butyrate in presence of the zinc-copper couple, crystallises from alcohol in long, slender needles

which melt at 71° and are soluble to a slight extent in light petroleum, and more readily in benzene or ether; in boiling ether, the ester has the normal molecular weight.

β-Hydroxy-β-p-anisyl-αα-dimethylpropionic acid,

$$OMe \cdot C_6H_4 \cdot CH(OH) \cdot CMe_2 \cdot CO_2H,$$

obtained by hydrolysing the ethyl ester, separates from alcohol, ether, or benzene in colourless crystals melting at 110°; it is slightly soluble in water and has the normal molecular weight in boiling ether. The corresponding *potassium* ($+H_2O$), *sodium* ($+4H_2O$), and *barium* ($+4H_2O$) salts are slightly soluble in water; the calcium, magnesium, zinc, manganese, nickel, cobalt, silver, mercury, lead, and copper salts are crystalline and the iron salt is flocculent, all being slightly soluble in water.

When distilled with sulphuric or hydrochloric acid or when heated in a sealed tube with dilute sulphuric, hydrochloric, or hydriodic acid, one half of the acid is decomposed into the methyl derivative of *iso*butenylphenol, carbon dioxide, and water, and the other half into anisic and *iso*butyric acids. With dilute alkaline permanganate solution, the acid undergoes partial decomposition, anisic acid occurring among the products.

These decompositions of β-hydroxy-β-*p*-anisyl-αα-dimethylpropionic acid indicate that it consists of a mixture of two isomerides. When added to the solution, a strychnine salt yields star-shaped crystals melting at 90° and prisms melting at 190°, and the acid obtained from the strychnine salt melts at 130°. T. H. P.

Condensation of Benzil with Resorcinol. HANS VON LIEBIG (*Ber.*, 1903, **36**, 3046—3051).—When molecular quantities of benzil and resorcinol are heated for some time at 150—230°, *dihydroxytriphenylmethanecarboxylic lactone*, $C_{20}H_{14}O_3$, is formed to the extent of 80—90 per cent. Analyses agree better with the formula $C_{40}H_{30}O_6$. It separates from alcohol in monoclinic crystals which melt at 168°. Its *monoacetyl* derivative separates from alcohol in monoclinic leaflets, which melt at 120° and are hydrolysed by alcoholic alkali. Its *diacetyl* derivative separates from alcohol in leaflets, which melt at 161° and are hydrolysed by alcoholic alkali. Its *dibenzoyl* derivative separates from benzene in glistening crystals and melts at 208°. The *acid*, $C_{40}H_{34}O_8,2H_2O$, crystallises from water in needles; the *sodium* salt, containing $4H_2O$, separates from water in hexagonal prisms, the *potassium* salt, containing $4H_2O$, in long needles, the *ammonium* salt, containing $2H_2O$, in needles; the potassium salt separates from alcohol in tetragonal pyramids and the ammonium salt in prisms, and they crystallise with 2EtOH respectively. The *hexasodium* salt and the *hexapotassium* salt form needles.

When the lactone is submitted to dry distillation or when it is distilled with zinc dust or with soda-lime, it forms diphenylmethane; when oxidised by strong oxidising agents, it forms benzophenone and benzoic acid. Heating in a sealed tube with hydrochloric acid converts it into a red substance, which dissolves in alkali with a green fluorescence. Other fluorescent substances are also produced when the lactone is heated at 300° and the mass then acted on by potassium hydroxide.

Traces of four other substances were also obtained when benzil and

resorcinol were heated at 150—230°; two of them were possibly resorcinol ethers. A. McK.

Condensation of Benzil with Resorcinol. Hans von Liebig and Hugo Hurt (*Ber.*, 1903, 36, 3051—3054. Compare preceding abstract).—Molecular quantities of benzil and resorcinol, when heated with powdered potassium hydroxide or potassium carbonate for 20 minutes at 130—150°, form six substances: (1) a dark red powder, $C_{40}H_{36}O_6$, soluble in alkalis and in alcohol to form a red solution, which exhibits a green fluorescence, (2) a brick-red powder, $C_{40}H_{28}O_5$, of which the potassium and sodium salts, the sulphate, hydrochloride, picrate, and diacetyl derivative are described, (3) benzoic acid, (4) dihydroxytriphenylmethanecarboxylic lactone, (5) resorcylic acid, (6) a substance, $C_{20}H_{14}O_5$, which melts above 330°. A. McK.

Action of Nitrous Acid on the Oximes of the Santonin Series; Santolic Acid. Luigi Francesconi and F. Ferrulli (*Gazzetta*, 1903, 33, i, 188—206. Compare Francesconi and Angelucci, Abstr., 1902, i, 35, and Francesconi and Vendetti, Abstr., 1902, i, 545).—Pernitrososantonin (*loc. cit.*) can be obtained by the action of sodium nitrite on santonin in acetic acid solution more readily than with amyl nitrite; when reduced by means of sodium amalgam in acetic acid solution, pernitrososantonin yields *iso*hyposantonin, already prepared by Gucci (Abstr., 1890, 902) and by Grassi-Cristaldi (Abstr., 1890, 904) by the reduction of santoninoxime or santonin phenylhydrazone. Pernitrososantonin is not acted on by acetic anhydride even when fused with sodium acetate, but by the action of gaseous hydrogen chloride on its alcoholic solution an unstable red compound melting at 115° is obtained.

Santonic acid resembles santonin in not reacting directly with nitrous acid, but it yields a *hydrazone*, $C_{15}H_{20}O_3{:}N{\cdot}N{:}C_{15}H_{20}O_3$, separating from ethyl acetate in silky needles melting, with previous softening, at 206—207°; this is optically active, $[\alpha]_D$ −86·75°, and dissolves slightly in alcohol or acetone and more readily in acetic acid or ethyl ether; it dissolves also in solutions of the alkali carbonates, from which it is precipitated unaltered by the addition of hydrochloric acid.

Santonic acid semicarbazone, $C_{15}H_{20}O_3{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, is deposited from a mixture of ether and ethyl acetate in crystals melting at 183—185° with previous softening; it is readily soluble in ethyl acetate, acetic acid, alcohol, acetone, or alkali carbonate solutions, and, to a less extent, in ether, benzene, or chloroform, and has $[\alpha]_D$ +13·39°.

When acted on by nitrous acid, santonic acid oxime does not yield a pernitroso-derivative, but forms *hydroxamsantolic anhydride*,

$$\begin{array}{l} CMe_2{\cdot}CH{-}CH_2{\cdot}CO \\ CMe{-}CH{-}CH_2{\cdot}CH \\ C(OH){:}N{\cdot}O{\cdot}CO{\cdot}CHMe, \end{array}$$

which crystallises from alcohol in long, shining prisms melting at 226—227°, and in alcoholic solution at 25° has $[\alpha]_D$ −214·33°; it is readily soluble in ether and to a slight extent in chloroform, benzene,

or acetic acid; with ferric chloride, it gives the violet coloration yielded by the hydroxamic acids, but it does not react with acetic anhydride nor does it give Liebermann's reaction; it is insoluble in alkali carbonates, but dissolves in alkali hydroxide solutions, giving a liquid from which acetic acid does not precipitate it immediately, but only on concentration; it is dissolved and decomposed by hydrochloric acid, the solution reducing Fehling's solution; it yields a *barium* salt, $C_{30}H_{40}O_8N_2Ba,H_2O$.

Santolic acid, $\begin{matrix} CMe_2\cdot CH\cdot CH_2\cdot CO \\ CO_2H\cdot CMe{-}CH\cdot CH_2\cdot CH\cdot CHMe\cdot CO_2H \end{matrix}$, obtained, together with hydroxylamine, when hydroxamsantolic anhydride is heated with dilute sulphuric acid, separates from ether in large, shining, rhombohedral crystals melting at 166—167°; it is readily soluble in alkali carbonate solutions and to a less extent in ethyl acetate; it has $[\alpha]_D$ +90·65° in alcohol at 27°. Its *ethyl* and *methyl* esters are oils. The *barium* (with H_2O) and *silver* salts were prepared. With hydroxylamine, it yields: (1) a *compound*, apparently the oxime, which forms pale yellow, cubical crystals, melting and decomposing at 202—205°, and is soluble in alcohol, ether, or ethyl acetate, and to a slight extent in acetic acid; it dissolves in dilute hydrochloric acid, and the solution reduces Fehling's solution in the cold; (2) a *compound*, possibly a transformation product of the oxime, which contains nitrogen and melts and decomposes at 179—181°; it is readily soluble in alcohol, ether, or ethyl acetate and to a less degree in acetic acid; when decomposed with hydrochloric acid, it does not reduce Fehling's solution.

Under the action of nitrous acid, the oxime of ethyl ethylsantonate is hydrolysed, yielding ethyl santonate.

Neither santonic acid oxime, santolic acid, nor hydroxamsantolic anhydride yields any coloration with ferric chloride, but the barium salt of hydroxamsantolic anhydride gives a violet coloration.

T. H. P.

Constitution of Derivatives of Santonin. LUIGI FRANCESCONI (*Ber.*, 1903, 36, 2667—2669).—A criticism of Wedekind (this vol., i, 542).

W. A. D.

Behaviour of Methyl $\Delta^{2,5}$-Dihydroterephthalate at High Temperatures and in presence of Spongy Platinum. EMIL KNOEVENAGEL and B. BERGDOLT (*Ber.*, 1903, 36, 2857—2860).—Methyl $\Delta^{2,5}$-dihydroterephthalate, when heated, yields a mixture of methylterephthalate and methyl *cis*- and *trans*- hexahydroterephthalates. Thus whilst the conversion of 1 gram of the dihydro-ester into methyl terephthalate should cause the separation of 113 c.c. of hydrogen, only 1·4 c.c. were obtained at 140°, and 18 c.c. at 230°; the hexahydro-esters were separated from the decomposition product by fractional crystallisation and were further identified by conversion into the corresponding hexahydroterephthalic acids.

T. M. L.

A Peculiar Case of Isomerism. GEORG SCHROETER and HANS MEERWEIN (*Ber.*, 1903, 36, 2670—2676).—When *o*-nitro-β-phenylglutaric acid dissolved in ammonia is subjected to the action of hydrogen sulphide at 40—50°, it is not reduced, but converted into an isomeric substance, iso-o-*nitro-β-phenylglutaric acid*, which crystallises from water in large, flat, brittle prisms and melts at 204·5°. The nature of this substance and its derivatives cannot be explained by any constitutional formula differing from that of the parent substance, because all such formulæ necessitate a hydroxyl group which cannot be detected experimentally; neither is the isomerism apparently stereochemical. That the two *o*-nitrophenylglutaric acids do not differ by the isomerism of ortho-derivatives, presupposed by Kekulé's formula for benzene, is shown by the fact that the *o*:*o*-dinitro-derivatives prepared from the two acids are not identical. The molecular weights of the two acids and their derivatives are also identical, and therefore the difference between them is not due to polymerism.

Methyl iso-o-*nitro-β-phenylglutarate*, $NO_2 \cdot C_6H_4 \cdot CH(CH_2 \cdot CO_2Me)_2$, crystallises from ether in hexagonal prisms and melts at 65·5°. iso-o-*Nitro-β-phenylglutaric anhydride* crystallises from benzene in lustrous white needles and melts at 130—131°, whilst the *anhydride* of the normal acid melts at 106°; with ammonia, the two anhydrides give o-*nitro-β-phenylglutaramic acids*, melting respectively at 142° and 156°. With aniline, the normal anhydride gives an oil, and the *iso*anhydride an *anilic acid*, $NO_2 \cdot C_6H_4 \cdot CH(CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO \cdot NHPh$, melting at 139°.

On nitration with a mixture of fuming nitric acid and sulphuric acid, the normal acid gives a 2:6-*dinitro-β-phenylglutaric acid*, which crystallises from water in spherular aggregates and melts at 168—169°; the isomeric iso-2:6-*dinitrophenyl-β-glutaric acid* separates from water in monoclinic prisms and melts at 181°.

When 2:4-dinitro-β-phenylglutaric acid is reduced with cold hydrogen sulphide in cold ammoniacal solution, it gives *ammonium hydrogen* p-*hydroxylamino*-o-*nitro-β-phenylglutarate*,

$$OH \cdot NH \cdot C_6H_3(NO_2) \cdot CH(CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO \cdot ONH_4$$

(compare Abstr., 1902, i, 544), which crystallises from water in monoclinic prisms, and, on acidifying its solution, is converted into the *dibasic acid*, $C_{11}H_{12}O_7N_2$, which forms yellow needles and melts and decomposes at 165°; when this acid is boiled with hydrochloric acid, it yields the *azoxy-acid*, $ON_2[C_6H_3(NO_2) \cdot CH(CH_2 \cdot CO_2H)_2]_2$, which is a sparingly soluble micro-crystalline powder.

When the reduction of 2:4-dinitro-β-phenylglutaric acid with ammonium sulphide is effected at 50°, p-*amino*-iso-o-*nitro-β-phenylglutaric acid* is obtained in fan-like aggregates of red crystals melting at 185°; that the acid corresponds with *iso-o*-nitro-β-phenylglutaric acid and not with the normal acid is shown by the fact, that on eliminating the amino-radicle, it affords this acid melting at 204·5°.

W. A. D.

Behaviour of β-Diphenylsuccinonitrile at High Temperatures and in presence of Spongy Palladium. EMIL KNOEVENAGEL and B. BERGDOLT (*Ber.*, 1903, 36, 2861—2863).—When heated at 180°, *s*-β-

diphenylsuccinonitrile, $CN\cdot CHPh\cdot CHPh\cdot CN$, is converted into α-phenylcinnamonitrile, $CHPh{:}CPh\cdot CN$, and hydrogen cyanide. In presence of spongy palladium, a partial decomposition also occurs into dicyanostilbene, $CN\cdot CPh{:}CPh\cdot CN$, and hydrogen; the hydrogen is not liberated as such, but reduces a part of the diphenylsuccinonitrile to benzyl cyanide. Ten grams of the nitrile gave 3·5 grams of benzyl cyanide, 2 grams of dicyanostilbene, 3 grams of α-phenylcinnamonitrile and 0·38 gram of hydrogen cyanide. T. M. L.

Preparation of Phenylglycine-*o*-carboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 143902).—The method described in the former patent (this vol., i, 754) may be modified by using oxalyldiglycine in place of glycine. Oxalyldiglycine and *o*-chlorobenzoic acid are boiled with a solution of alkali carbonate and copper powder, and the phenylglycine-*o*-carboxylic acid is precipitated by pouring the hot solution into dilute mineral acid. C. H. D.

Action of Chloroacetamide on some Aromatic Amines. AUGUSTE L. LUMIÈRE and F. PERRIN (*Bull. Soc. chim.*, 1903, iii, 30, 966—968).—The following compounds have been prepared by the action of chloroacetamide on appropriate amino-compounds.

Phenylglycine-m-*carboxylodiamide*, $NH_2\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2$, crystallises in colourless needles, melts at 201—202°, is soluble in warm water, and less so in cold. p-*Chlorophenylglycinamide*,

$$NH_2\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4Cl,$$

melts at 125—126° and is soluble in warm, less so in cold water. *Phenolaminoacetamide*, $NH_2\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot OH$. The *meta*-derivative melts at 145° and the *para*-compound at 135—136°. The *methyl ether* of the latter melts at 145—146° and the *ethyl ether* at the same temperature, whilst the *methyl* and *ethyl ethers* of the *ortho*-isomeride melt respectively at 153—154° and 161—162°.

β-Naphthylaminoacetamide, $NH_2\cdot CO\cdot CH_2\cdot NH\cdot C_{10}H_7$, melts at 164—165°. *Phenylenebisaminoacetamide*, $C_6H_4(NH\cdot CH_2\cdot CO\cdot NH_2)_2$. The *meta*-derivative melts at 196—197° and the *para*-isomeride at 250—252°. p-*Dimethylanilinoaminoacetamide*,

$$NH_2\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot NMe_2,$$

melts at 159—160°. *Antipyrineaminoacetamide*,

$$NH_2\cdot CO\cdot CH_2\cdot NH\cdot \begin{array}{l} CMe\cdot NMe \\ \| \\ C\text{——}CO \end{array}\!\!>NPh,$$

crystallises in pale yellow needles, melts at 194—195°, and is readily soluble in warm, less so in cold water. T. A. H.

Preparation of Tetraiodophenolphthalein. KALLE & CO. (D.R.-P. 143596).—Phenolphthalein is dissolved in sodium hydroxide, and a slight excess of iodine chloride and hydrochloric acid is slowly added. The precipitate obtained is purified by dissolving in alcohol and precipitating by acid. The phenolphthalein and iodine chloride may also be employed in 50 per cent. acetic acid solution.

C. H. D.

Constitution of Phthalein Salts. Richard Meyer and Oskar Sprengler (*Ber.*, 1903, 36, 2949—2967).—The examination of a number of quinolphthalein derivatives has disproved the assumption of a meta-quinonoid constitution, and made a lactonoid structure for such compounds probable. *Ethyl quinolphthalincarboxylate*,

$$CO_2Et\cdot C_6H_4\cdot CH{<}{\genfrac{}{}{0pt}{}{C_6H_3(OH)}{C_6H_3(OH)}}{>}O,$$

forms colourless crystals melting at 188—189° and easily soluble in alcohol. *Quinolphthaleindimethyl ether*, $\genfrac{}{}{0pt}{}{C_6H_4}{CO\cdot O}{>}C{<}{\genfrac{}{}{0pt}{}{C_6H_3(OMe)}{C_6H_3(OMe)}}{>}O$, prepared by direct methylation of the phthalein with methyl iodide, crystallises in colourless granules melting at 200°; the corresponding *diethyl ether* melts at 164°. The formation of these ethers affords evidence in favour of the lactonoid formula. The *anilide*,

$$CO{<}{\genfrac{}{}{0pt}{}{C_6H_4}{NPh}}{>}C{<}{\genfrac{}{}{0pt}{}{C_6H_3(OH)}{C_6H_3(OH)}}{>}O,$$

crystallises from alcohol in white needles melting at 305° and dissolves without coloration in alkali hydroxides. Its *dimethyl* ether, which is insoluble in alkali hydroxides, melts at 183°. These two compounds undoubtedly possess a lactonoid structure, and their conversion into quinolphthaleindimethyl ether, when acted on by alcohol and sulphuric acid, proves the same for this compound also.

When hydroxylamine acts on quinolphthalein, it forms three oximes: a colourless *α-oxime*, crystallising in plates, which melts at 268—269° and dissolves in alkali hydroxides without coloration or fluorescence, and probably has a lactonoid constitution. It forms a *triethyl ether* melting at 158—159°. The *β*- and *γ-oximes* are yellow and decompose on heating. The *β*-oxime dissolves in alcohol, showing an intense green fluorescence; it is easily converted into the γ-oxime, which is insoluble in alcohol and does not fluoresce; these two oximes are probably stereoisomerides. Phenolphthalein oxime forms a *trimethyl ether*, which crystallises in colourless needles melting at 145°, a *triethyl ether* melting at 142—143°, and a *tribenzyl ether* crystallising from alcohol in colourless plates and melting at 134°. Alcoholic potash converts the trimethyl into a *dimethyl ether*, which crystallises in glistening needles melting at 178°. When heated with mineral acids, the trimethyl ether is resolved into *p*-methoxybenzoylbenzoic acid and *p*-aminoanisole. E. F. A.

Amino-acids. S. P. L. Sörensen (*Chem. Centr.*, 1903, ii, 33—35; from *Compt. rend. trav. Labor. Carlsberg, Kopenhagen*, 6, 1—63).—*Ethyl phthaliminomalonate*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}N\cdot CH(CO_2Et)_2$, prepared by heating potassium phthalimide with ethyl bromomalonate at 100—120°, crystallises from alcohol in colourless, microscopic prisms, melts at 73·8—74°, and is easily hydrolysed to the *tricarboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH(CO_2H)_2,$$

which was not further investigated. The *sodium* derivative,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}N\cdot CNa(CO_2Et)_2,$$

prepared from the ester and sodium ethoxide, is freed from alcohol by

heating it at 130—140°; on boiling it with benzyl chloride for 6 hours, it yields *ethyl benzylphthaliminomalonate*,

$$C_6H_4:(CO)_2:N\cdot C(CO_2Et)_2\cdot CH_2Ph,$$

which crystallises from alcohol in colourless prisms, melts at 105—106°, and is hydrolysed by aqueous sodium hydroxide to *phthalaminobenzylmalonic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C(CO_2H)_2\cdot CH_2Ph$, which melts and decomposes at 160—165°. When boiled with concentrated hydrochloric acid, this substance is resolved into phthalic acid and 80 per cent. of the theoretical quantity of *i*-phenylalanine.

Ethyl γ-cyanopropylphthaliminomalonate,

$$C_6H_4<{CO \atop CO}>N\cdot C(CO_2Et)_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN,$$

prepared by heating γ-chlorobutyronitrile with ethyl sodiophthaliminomalonate for 3—4 hours at 160—165°, separates from alcohol in colourless crystals and melts at 91°; on hydrolysis with alkalis, it gives the *tetracarboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C(CO_2H)_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H,$$

which is decomposed by hydrochloric acid with formation of *a-aminoadipic acid*, $CO_2H\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$. The latter is obtained from aqueous solutions above 20° in anhydrous crystals, but at 0° a *monohydrate* separates; the anhydrous form crystallises in lamellæ or microscopic leaflets and melts at 204—206° (corr.); the monohydrate consists of needles. The *benzoyl* derivative,

$$CO_2H\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NHBz,$$

forms colourless, microscopic prisms and melts at 184° (corr.).

Ethyl phthalimino-γ-phthaliminopropylmalonate,

$$C_6H_4:(CO)_2:N\cdot C(CO_2Et)_2\cdot[CH_2]_3\cdot N:(CO)_2:C_6H_4,$$

prepared by heating γ-bromopropylphthalimide with ethyl sodiophthaliminomalonate at 175°, crystallises from alcohol in yellow needles, melts at 125°, and is hydrolysed by alkali to the *tetracarboxylic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C(CO_2H)_2\cdot[CH_2]_3\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$; this can be obtained anhydrous when it melts at 192—193° (corr.), or as a hydrate with $4H_2O$, which melts at 101—106°. When the tetracarboxylic acid is heated with hydrochloric acid, it gives αδ-diaminovaleric acid, which can readily be isolated as the dibenzoyl derivative, identical with *i*-ornithuric acid.

On reducing the foregoing ethyl cyanopropylphthaliminomalonate with sodium in alcoholic solution, the *compound*,

$$C_6H_4:(CO)_2:N\cdot C(CO_2Et)_2\cdot[CH_2]_3\cdot CH_2\cdot NH_2,$$

is obtained, which by concentrated hydrochloric acid is transformed into *i-αε-diaminohexoic acid* (*i*-lysine). W. A. D.

Combination of Formaldehyde with Indigotin. GUSTAV HELLER [with FRIEDRICH MICHEL] (*Zeit. Farb. Text. Chem.*, 1903, 2, 329—332).—*Ethyl methylenediphenylglycinetetracarboxylate*,

$$CH_2[C_6H_3(CO_2Et)\cdot NH\cdot CH_2\cdot CO_2Et]_2,$$

prepared by heating a mixture of phenylglycinecarboxylic acid, aqueous formaldehyde, absolute alcohol, and alcohol saturated with hydrogen chloride for 6—8 hours in a reflux apparatus, crystallises from ether in slender needles, melts at 113—114°, and is easily hydrolysed by alcoholic potassium hydroxide to the corresponding

tetracarboxylic acid, $C_{19}H_{18}O_8N_2$. The analogous *methyl* ester,

$$CH_2[C_6H_3(CO_2Me)\cdot NH\cdot CH_2\cdot CO_2Me]_2,$$

prepared similarly by using methyl alcohol, crystallises in long, thin needles and melts at 142—143°.

Methyleneindigotin, $C_{17}H_{10}O_2N_2$, is prepared by fusing the foregoing tetracarboxylic acid with potassium hydroxide, first at 240° and subsequently at a higher temperature, dissolving in water in an atmosphere of hydrogen, and precipitating by a current of air; it is very sparingly soluble in all solvents and has a greener colour than indigotin. It is sulphonated much less readily than indigotin, the *sulphonic acid*, $C_{17}H_{10}O_5N_2S$, only being obtained after heating it with concentrated sulphuric acid for several hours on the water-bath; this substance has no affinity for wool. Like indigotin, methyleneindigotin is easily reduced by sodium hyposulphite or zinc dust and aqueous sodium hydroxide to a *leuco*-derivative, which, however, could not be obtained crystalline; it is readily converted into its *acetyl* or *benzoyl* derivative, but these substances are insoluble in all solvents.

Methyleneisatin, obtained by oxidising methyleneindigotin with dilute nitric acid, is a red powder which cannot be obtained crystalline.

Benzylideneindigotin, prepared by fusing with alkali the product obtained by the interaction of phenylglycinecarboxylic acid and benzaldehyde in presence of hydrochloric acid at 60—80°, closely resembles the methylene derivative. W. A. D.

Silver and Mercury Compounds of certain Oximes. Transformation of Stereoisomeric Oximes. LUIGI FRANCESCONI and E. PIAZZA (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 128—137).—The authors have examined the compounds formed by certain oximes with silver nitrate and with mercurous nitrate, their results being as follows.

Addition of concentrated aqueous silver nitrate to a dilute nitric acid solution of camphoroxime yields a *compound*, $C_{20}H_{34}O_5N_3Ag$, which separates from benzene solution in shining crystals melting at 157—158°, and is stable towards light; it is soluble in alcohol or ether and, when crystallised from either of these solvents, is rapidly blackened in the light; it has an abnormally high molecular weight in freezing benzene and, when treated with alkali solution or boiling water, yields camphoroxime again. With mercurous nitrate in dilute nitric acid, this oxime yields a *compound*, $C_{10}H_{17}O_7N_3Hg_2$, in the form of a white, crystalline powder not acted on by light and melting and decomposing at 136°; it is almost insoluble in organic solvents and is decomposed by hot water, giving metallic mercury and a resinous product, whilst with dilute alkali hydroxide solutions it yields camphoroxime.

anti-Benzaldoxime yields a *compound*, $C_{14}H_{14}O_5N_3Ag$, which, when crystallised from alcohol, melts at 129—130°; it is slightly soluble in ether or benzene, and with water gives the original oxime, whilst the action of alkali gives rise to the isomeric oxime. Mercurous nitrate yields, with this oxime, thin, shining scales which have the *composition* $C_7H_7O_4N_2Hg$ and melt and decompose at 92°; water

and alkali hydroxide act in the same way as they do on the silver nitrate compound.

m-Dimethyl-*anti*-benzaldoxime also yields a *compound* with silver nitrate, melting at 150°.

With silver nitrate, a mixture of stereoisomeric *iso*nitrosocamphors, melting at 128—132°, yields a *compound*, $C_{20}H_{30}O_7N_3Ag$, which separates from benzene in crystals melting and decomposing at 136—137°; it is only slowly darkened under the action of light and is soluble in alcohol or ether; by treating with dilute alkali hydroxide solution, filtering, and passing carbon dioxide through the filtrate, the *iso*nitrosocamphor melting at 152—154° is obtained; the latter may hence be separated from its stereoisomeride by means of the silver nitrate compound. With mercurous nitrate, this mixture of stereoisomerides gives a *compound*, $C_{20}H_{30}O_{13}N_5Hg_3$, which melts and decomposes at 132° and yields the *iso*nitrosocamphor melting at 152—154° when treated with an alkali hydroxide and carbon dioxide.

Similar double compounds could not be obtained with trioximinomethylene, acetoxime, acetaldoxime, santoninoxime, quinonemonoxime, quinonedioxime, or camphordioxime; salicylaldoxime forms a compound with mercurous nitrate, but not with silver nitrate.

The author supposes that, in the nitric acid solution of *anti*-benzaldoxime, there exists the free *anti*-oxime, the nitrate of the *syn*-oxime and nitric acid, and that, on addition of silver nitrate, the silver salt of the *syn*-stereoisomeride crystallises out together with 1 mol. of the nitrate of the *syn*-oxime. For the silver nitrate compounds formed by the oximes he hence proposes the structure:

$$R\cdot\overset{\displaystyle H}{\overset{|}{C}}\!:\!NOAg\cdot R\cdot\overset{\displaystyle H}{\overset{|}{C}}\!:\!NOH,HNO_3.$$

Formulæ are also suggested for the various mercury compounds.

T. H. P.

Cyclic Compounds. Oxidation of 2-Methyl*cyclo*hexanone. WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 381—389).—On oxidising 2-methyl*cyclo*hexanone, neither Bouveault and Tétry (Abstr., 1901, i, 364) nor Speransky (Abstr., 1902, i, 384) could obtain any trace of α-methyladipic acid, but by employing concentrated nitric acid as the oxidising agent, the author obtains as main product about equal proportions of α- and β-methyladipic acids, while *i*-pyrotartaric acid is formed also in small amount T. H. P.

Reduction of Benzylidene-α-nitroacetophenone. HEINRICH WIELAND (*Ber.*, 1903, **36**, 3015—3020).—Benzylidene-α-nitroacetophenone, $CHPh\!:\!CBz\cdot NO_2$ (this vol., i, 767), is reduced by stannous chloride and hydrochloric acid in methyl alcoholic solution to *iso*nitrosobenzylacetophenone, $CH_2Ph\cdot CBz\!:\!N\cdot OH$, identical with that prepared by Schneidewind (Abstr., 1888, 704) from benzylacetophenone and amyl nitrite, but crystallising in colourless tablets; probably the first product is the hydroxylamine, $CHPh\!:\!CBz\cdot NH\cdot OH$, which then undergoes isomeric change. When reduced with zinc dust and hydrochloric acid in methyl alcoholic solution, it yields a *polymeride* of

the amine, $CHPh:CBz\cdot NH_2$, which decomposes at 92° and yields ammonia when boiled with acids or alkalis. Another reduction product is a *compound*, $C_{30}H_{26}O_6N_2$, which crystallises from acetic acid in minute, colourless needles, melts and decomposes at 218°, and probably has the constitution $\begin{array}{l}CHPh\cdot CH(NO_2)\cdot CPh\cdot OH \\ | \qquad\qquad\qquad\quad | \\ CHPh\cdot CH(NO_2)\cdot CPh\cdot OH\end{array}$, since it is neither oxidised by chromic acid nor hydrolysed by mineral acids; it dissolves unchanged in alkalis like a nitroparaffin, is reduced to a base by stannous chloride and hydrochloric acid, and has the high melting point and sparing solubility of a polymeric compound. T. M. L.

Preparation of ψ-Ionone Hydrate. Pierre Coulin (D.R.-P. 143724).—When sulphuric or phosphoric acid is gradually added to ψ-ionone cooled by means of a freezing mixture, a hydrate is formed. The quantity of acid added must be less than that required to convert the ψ-ionone into ionone. *ψ-Ionone hydrate*, $C_{13}H_{22}O_2$, is a syrupy yellow liquid, almost without odour, and, unlike ionone and ψ-ionone, is not volatile in steam. It boils at 176—178° under 9 mm. pressure, has a sp. gr. 0·960 at 15° and 0·957 at 20°, and readily forms a *semicarbazone* melting at 144° when crystallised from benzene.
C. H. D.

Formation of a 1:2-Dioxime by addition of N_2O_3 to a Carbon Double Linking. Heinrich Wieland (*Ber.*, 1903, 36, 3020—3023).—By the action of sodium nitrite on a mixture of acetic acid and anethole, $OMe\cdot C_6H_4\cdot CH:CHMe$, there is produced the glyoxime peroxide, $\begin{array}{l}OMe\cdot C_6H_4\cdot C:N\cdot O \\ \qquad\qquad\quad | \qquad | \\ \qquad\quad CH_3\cdot C:N\cdot O\end{array}$, and the *amphi*-dioxime of methylanisyl-*o*-diketone, $\begin{array}{l}OMe\cdot C_6H_4\cdot C:NOH \\ \qquad\qquad\quad | \\ \qquad\quad CH_3.C:NOH\end{array}$ (Boeris, Abstr., 1894, i, 72). When the dioxime is heated with 25 per cent. sulphuric acid, it yields hydroxylamine and an iso*nitrosoketone*, probably

$$OMe\cdot C_6H_4\cdot CO\cdot CMe:N\cdot OH,$$

which crystallises from benzene in pointed, glistening tablets, melts at 128°, dissolves in alkalis to a yellow solution, and is reprecipitated in minute needles on the addition of acids. T. M. L.

Behaviour of Benzoin at High Temperatures and in presence of Catalytic Agents. Emil Knoevenagel and A. Tomasczewski (*Ber.*, 1903, 36, 2829—2848).—When heated, benzoin undergoes a complex decomposition, the chief products being benzil, benzophenone, and benzene, and minor products, benzaldehyde, water, and unsaturated hydrocarbons. The main reaction is probably $OH\cdot CHPh\cdot COPh = COPh\cdot COPh + H_2$, hydrogen being liberated as in the case of benzhydrol (see this vol., i, 820). Benzophenone might then be produced according to the equation $COPh\cdot COPh = COPh_2 + CO$, but this action takes place only to a very slight extent, and it is more probable that benzhydrol is an intermediate product, $OH\cdot CHPh\cdot COPh = OH\cdot CHPh_2 + CO = COPh_2 + CO + H_2$. Benzene might be produced directly from benzoin, $C_6H_5\cdot CH(OH)\cdot CO\cdot C_6H_5 = 2C_6H_6 + 2CO$, or

benzaldehyde might be an intermediate product. The decomposition is greatly facilitated by catalytic agents, the volume of gas liberated from 2 grams of benzoin at 293° in 6 hours being 1·3 c.c. when heated alone, and in presence of catalysts, silver, 1·0 c.c.; copper, 2·3 c.c.; nickel, 6·2 c.c.; gold, 12·1 c.c.; platinum, 124·2 c.c.; and palladium, 295·3 c.c. A detailed examination was made of the catalytic action of platinum and palladium, which were found to produce altogether different effects. Thus at 300°, with 2 grams of benzoin heated for 6 hours, platinum gave 76 c.c. of hydrogen, rising to 145·5 c.c. at 358°, whilst palladium gave 40·4 c.c., rising to 58·6 c.c.; but whilst the volume of carbon monoxide *increased* from 14·7 to 50·6 c.c. in presence of platinum, it *decreased* from 272·2 to 74·0 c.c. in presence of palladium, when the temperature was raised from 300 to 360°; palladium has thus a very remarkable power of causing a separation of carbon monoxide at low temperatures, but at 360° is little better than platinum, whilst platinum is much more efficient in promoting the separation of hydrogen, especially at high temperatures. Another important difference between the two catalysts is that the liberation of gas in presence of palladium is nearly complete in the first half-hour, whilst in presence of platinum the action is by no means complete at the end of 7 hours.

Dilution of the benzoin retards the decomposition, the volume of gas liberated from 2 grams of benzoin in seven hours in presence of 0·15 gram of platinum being reduced from 177·4 c.c. to 65·9, 119·0, and 127·9 c.c. by admixture with 10 grams of benzil, benzophenone, and phenanthrene respectively. It is, however, noteworthy that benzophenone and phenanthrene retard the liberation of carbon monoxide especially, whilst benzil retards the liberation of hydrogen.

T. M. L.

Mono-ethers of Quinonedioximes. Riccardo Oliveri-Tortorici (*Gazzetta*, 1903, 33, i, 237—240). — *Benzoylbenzoquinonedioxime*, $OH\cdot N:C_6H_4\cdot NO\cdot COPh$, prepared by the interaction of benzoquinonedioxime and benzoyl chloride in pyridine solution, separates from alcohol in minute, brick-red crystals, which show no definite melting point, but begin to decompose gradually at about 160°; it dissolves readily in alkali solutions; with benzoyl chloride, it yields the corresponding *dibenzoyl* derivative, which is insoluble in alkali solutions.

Benzoyltoluquinonedioxime, $OH\cdot N:C_6H_3Me\cdot NO\cdot COPh$, prepared in an analogous manner, separates from alcohol in minute, yellow crystals, which rapidly become brown in the air and melt and decompose at 180°; it is very soluble in ammonia and alkali hydroxide solutions and moderately so in alcohol or ether; benzoyl chloride converts it into the corresponding *dibenzoyl* derivative, which decomposes at 196°.

Both these mono-ethers are stable towards potassium ferricyanide.

T. H. P.

Nitrosophenol Dyes. Herman Decker and Boris Solonina (*Ber.*, 1903, 36, 2886—2894).—The blue oxonium salt obtained by the action of nitric acid on thymol ethyl ether (Abstr., 1902, i, 767) melts

at 79° and not, as there stated, at 62—63°. The methyl and *n*-butyl ethers give the same reaction, but no crystalline product could be isolated. Dithymolylamine diethyl ether (*loc. cit.*) forms a *stannochloride*, $C_{24}H_{36}O_2NCl,SnCl_2,3H_2O$, crystallising in needles, and a *hydriodide* forming colourless needles rapidly becoming red. Boiling with acetic anhydride and sodium acetate produces an N-*acetyl* derivative, $NAc(C_6H_2MePr^{\alpha}\cdot OEt)_2$, melting at 89—90°, together with p-*acetylthymolyl*-p-*ethylthymolylamine*,

$$OEt\cdot C_6H_2MePr^{\alpha}\cdot NH\cdot C_6H_2MePr^{\alpha}\cdot OAc,$$

crystallising from alcohol—ethyl acetate in monoclinic tables melting at 122—123°. Alcoholic ferric chloride oxidises this acetyl compound to *thymoquinone*-p-*acetylthymolimide*, $O:C_{10}H_{12}:N\cdot C_{10}H_{12}\cdot OAc$, which is hydrolysed by heating with sodium hydroxide to Liebermann's dye (see later). Ferric chloride oxidises the diethyl ether of dithymolylamine to *thymoquinone-thymolimide ethyl ether*, $OEt\cdot C_{10}H_{12}\cdot N:C_{10}H_{12}:O$, dark red, monoclinic crystals, forming an *oxime* which crystallises from dilute alcohol in bright yellow needles melting at 124—125°. Boiling with dilute sulphuric acid decomposes the ethyl ether into thymoquinone and *p*-aminothymol ethyl ether. Stannous chloride reduces the quinone-ether to *dithymolylamine ethyl ether*,

$$OEt\cdot C_{10}H_{12}\cdot NH\cdot C_{10}H_{12}\cdot OH,$$

which readily absorbs oxygen, reforming the violet quinone-ether. In the course of ethoxyl determinations, *dithymolylamine hydriodide*, $NH_2I(C_{10}H_{12}\cdot OH)_2$, was obtained as small, cubic crystals. Thymoquinone-thymolimide (Liebermann's dye), $O:C_{10}H_{12}:N\cdot C_{10}H_{12}\cdot OH$, is best prepared by the action of sulphuric acid and sodium nitrite on thymol, the ammonium salt of dithymolylamine being produced at the same time. Acetyl chloride converts it into thymoquinone-acetylthymolimide. Ethyl sulphate also forms the ethyl ether described above, and the constitution of the dye is therefore definitely determined.

[With S. Gadomska.]—Other simpler nitrosophenol dyes have been examined, and the following regularities in the colour reactions of phenols with nitrous acid in concentrated sulphuric acid are pointed out: (1) phenols with open para-position form quinone-phenolimides, which give blue solutions in sulphuric acid, becoming red or violet on dilution, and cornflower-blue on addition of alkali. (2) A group of high molecular weight in the ortho-position to the para-hydrogen may prevent the reaction (carvacrol). Acid groups may have the same effect in any position (salicylic acid, *o*-nitrophenol). C. H. D.

Preparation of Alkylaminoanthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 144634. Compare this vol., i, 498).—In place of secondary fatty amines, primary amines may be allowed to react with substituted anthraquinones according to the method indicated in the earlier patents. The products obtained are strongly basic. α-*Methylaminoanthraquinone*, from methylamine and α-nitroanthraquinone, forms yellowish-red needles melting at 167°. α-*Methylamino-β-methylanthraquinone*, long, glistening needles, melts at 114°. α-*Benzylaminoanthraquinone*, orange-red leaflets melting at 188°. α-*Amylaminoanthraquinone*, brownish-red needles melting at 90°.

1 : 8-*Nitromethylaminoanthraquinone* separates from pyridine in garnet-red needles. 1 : 8-*Dimethyldiaminoanthraquinone* crystallises from pyridine in very long prisms with a green lustre; 1 : 5-*dimethyldiaminoanthraquinone* separates in large, golden needles. 1 : 4-*Hydroxymethylaminoanthraquinone*, from quinizarin, forms crystals with a bronze lustre. 1 : 4-*Bromomethylaminoanthraquinone*, from 1 : 4-bromonitroanthraquinone and methylamine, crystallises in brownish-red needles melting at 192°. 1-*Nitro*-4 : 5 : 8-*trimethyltriaminoanthraquinone* forms crystals with a bronze lustre.

The solubility and colour-reactions of these and many other similar derivatives are given in tabular form. C. H. D.

Dinitrosulphonic Acids of the Dialkyl Ethers of Anthrachrysone, Anthraflavic Acid, and *iso*Anthraflavic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 139425 and 143858).—Anthrachrysone reacts with methyl sulphate to form a dimethyl ether. When this ether is heated with fuming sulphuric acid until soluble in water, a disulphonic acid is obtained, which is converted by cold nitric acid into a dinitro-derivative. This treatment does not hydrolyse the alkyloxy-groups. The *potassium hydrogen* salt, $SO_3H\cdot C_{14}H_4O_2(OH)_2(OMe)_2(NO_2)_2\cdot SO_3K$, separates in ruby-red crystals, dissolving in water to an orange solution. Alkalis precipitate the vermilion normal salts. The dialkyl ethers of anthraflavic and *iso*anthraflavic acids may be sulphonated and nitrated in a similar manner. The *dimethyl ether*, $C_{14}H_6O_2(OMe)_2$, of *iso*anthraflavic acid forms yellow crystals melting at 215°. The *potassium hydrogen* salt of the dinitro-disulphonic acid, $SO_3H\cdot C_{14}H_2O_2(OMe)_2(NO_2)_2\cdot SO_3K$, crystallises in yellowish-red needles. C. H. D.

Derivatives of Chrysazin and of Hystazarin. H. SCHROBSDORFF (*Ber.*, 1903, **36**, 2936—2940. Compare Abstr., 1902, i, 773).—*Chrysazinamide*, $OH\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_3\cdot NH_2$, obtained by saturating chrysazin paste with ammonia at 0° and heating in sealed tubes at 145°, may be crystallised from alcohol, and dissolves in barium hydroxide solution. When the amino-group is removed, erythrohydroxyanthraquinone is formed.

Bromine at the ordinary temperature converts chrysazin into a *dibromo*-derivative, $C_{14}H_6O_4Br_2$, which crystallises from acetic acid in orange-yellow needles melting at 210—213°. A *tetrabromochrysazin* obtained by the action of bromine at 150° crystallises from benzene in orange-red needles melting at 295°, and is soluble in dilute alkalis. A *dihydroxychrysazin*, $C_{14}H_6O_2(OH)_4$, is formed when the dibromo-derivative is fused with potassium hydroxide; it crystallises in dark red needles, melts at 217°, and is soluble in dilute alkalis or concentrated sulphuric acid; it yields violet-coloured *barium* and *calcium* salts and furnishes dyes with the ordinary mordants. Its *tetra-acetyl* derivative forms pale yellow needles melting at 195°.

2 : 3-*Dihydroxyanthranol*, $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{CH}>C_6H_2(OH)_2$, obtained by

boiling hystazarin (Abstr., 1902, i, 548) with ammonia and zinc dust for 10 minutes, crystallises in yellowish-brown needles, melts at 282°, and dissolves in alkali hydroxides, yielding yellow solutions with a pale green fluorescence. The *acetyl* derivative, $C_{14}H_7(OAc)_3$, melts at 163—164° and on oxidation yields diacetylhystazarin.

Dibromohystazarin, $C_{14}H_4Br_2O_2(OH)_2$, obtained by the action of bromine at 150°, melts at 127—129° and forms dyes with the ordinary mordants.

1-*Nitrohystazarin*, $C_6H_4{<}{}^{CO}_{CO}{>}C_6H(OH)_2{\cdot}NO_2\,[NO_2:(OH)_2 = 1:2:3]$, is formed when a sulphuric acid solution of potassium nitrate is added to a solution of hystazarin in the same solvent; it crystallises from toluene and dissolves readily in alcohol, ether, or acetic acid. The 1 : 4-*dinitro*-derivative, obtained in a similar manner, dissolves in alkali hydroxides, yielding blue solutions, and also forms deep blue crystalline *barium* and *calcium* salts. J. J. S.

Chrysazin Derivatives. F. Wölbling (*Ber.*, 1903, 36, 2941—2942).—Chrysazin forms a somewhat sparingly soluble *potassium* derivative, $C_{14}H_7O_4K$, which crystallises in orange-red needles.

Chrysazindisulphonic acid forms a characteristic *potassium* salt, $C_{14}H_4O_2(OH)_2(SO_3K)_2$, which may be used for purifying the acid. It dissolves readily in water, but is thrown down as a crystalline precipitate on the addition of alcohol. When fused with potassium hydroxide, it yields *dihydroxychrysazin*, $C_{14}H_4O_2(OH)_4$, which is best purified by sublimation in a vacuum. It melts at 292°, dissolves in alkali hydroxides to blue solutions, and forms dyes with the ordinary mordants. Its *acetyl* derivative, $C_{14}H_4O_2(OAc)_4$, forms yellow needles melting at 238—240°. J. J. S.

Condensations with Citronellal. Hans Rupe and Walther Lotz (*Ber.*, 1903, 36, 2796—2802).—In order to study the influence on the optical properties of a double linking in the same chain as an asymmetric complex, condensation products of citronellal have been prepared. The condensation of citronellal with ethyl bromoacetate in presence of zinc gave rise chiefly to *iso*pulegol. Citronellal condenses with malonic acid in presence of pyridine, however, forming *citronellideneacetic acid*,

$$CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2Et,$$

a viscid, colourless and odourless liquid, boiling at 175·5—177·5° under 14 mm. pressure and remaining liquid at −20°. It has a sp. gr. 0·9326 at 20°/4° and $[\alpha]_D - 6{\cdot}49°$. The *methyl ester* is a fragrant, limpid liquid, boiling at 135—137° under 14 mm. pressure and having a sp. gr. 0·8177 at 20°/4° and $[\alpha]_D - 9{\cdot}56°$ in alcoholic solution. The acid combines with hydrogen bromide to form a *hydrobromide* and a *dihydrobromide*, both of which are viscous oils. Sulphuric acid forms a less volatile acid, which will be further investigated.

Citronellal condenses with acetone under the influence of dilute alkalis, forming *citronellideneacetone*,

$$CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COMe,$$

a colourless oil, boiling at 142—144·5° under 14 mm. pressure, and

having a sp. gr. 0·8737 at 20°/4° and $[\alpha]_D$ $-2·70°$. It combines with 2 mols. of semicarbazide to form a crystalline *compound*, $C_{15}H_{30}O_2N_6$, melting at 167°. The addition probably takes place at the double linking adjoining the carbonyl group. C. H. D.

Chemical Constituents from the Eucalypts. Henry G. Smith (*J. Roy. Soc. N.S. Wales*, 1902, 36, 61—70. Compare Abstr., 1901, i, 282).—Samples of the oil of *Eucalyptus Macarthuri* have been examined in which the geranyl acetate varies from 60 to 75 per cent. It is found that as the amount of the ester increases, the amount of the free geraniol present correspondingly diminishes. E. G.

Derivatives of Camphor. Angelo Angeli, Francesco Angelico, and V. Castellana (*Atti Real. Accad. Lincei*, 1903, [v], 12, i, 428—434).—When chloropernitrosocamphor is oxidised with potassium permanganate, it yields camphoric acid, whilst with concentrated sulphuric acid it forms *iso*camphenone with evolution of nitrous oxide and hydrogen chloride; dilute acids or alkalis act on it, giving nitrous oxide and chlorocamphor. With ammonia or a primary amine, it behaves similarly to all pernitroso-derivatives; thus, with hydroxylamine, it yields *chlorocamphoroxime*, $C_8H_{14}<\begin{matrix}C{:}N{\cdot}OH\\ |\\ CHCl\end{matrix}$, which forms large crystals melting at 127°. This compound dissolves unaltered in concentrated sulphuric acid, but when boiled for some time with dilute sulphuric acid it yields chlorocampholenonitrile; with nitrous acid, it gives chloropernitrosocamphor again. With ammonia, the latter gives the *chloroimine*, $C_8H_{14}<\begin{matrix}C{:}NH\\ |\\ CHCl\end{matrix}$, which begins to darken at about 200° without melting, and on treatment with dilute mineral acids is readily hydrolysed, forming chlorocamphor and ammonia. The chloropernitroso-compound reacts with semicarbazide acetate, yielding *chlorocamphorsemicarbazone*, $C_{10}H_{15}Cl{:}N_2H{\cdot}CO{\cdot}NH_2$, which melts at 183°.

Like other pernitroso-compounds, chloropernitrosocamphor is changed by alcoholic alkali hydroxide solution into the isomeric *isochloropernitrosocamphor*, $C_{10}H_{14}Cl{\cdot}N_2O_2H$, crystallising in needles melting at 75°, and of which the *potassium* derivative was prepared; *iso*chloropernitrosocamphor decomposes spontaneously, even at the ordinary temperature, into an oily mixture containing chlorocamphor, hydrogen chloride, nitroso-products, &c. By the action of dilute acids on *iso*chloropernitrosocamphor, or by the addition of excess of sodium carbonate to its sulphuric acid solution, it is converted into another isomeride, *ψ-chloropernitrosocamphor*, which forms large, yellow crystals melting at about 90°; the *picrate* separates from alcohol in yellow needles melting at 155°, and the *hydrochloride*, $C_{10}H_{15}ClN_2O_2,HCl$, forms white needles melting at 162°. It is a weak base and does not react with benzoyl or acetyl chloride, acetic anhydride, or phenylcarbimide; in alcoholic solution, it is stable towards permanganate, but on reduction with zinc and acetic acid it yields a base which reduces

Fehling's solution; when boiled with dilute sulphuric acid, it gives rise to Cazeneuve's chloronitrocamphor, the compound $C_8H_{14}<\begin{array}{l}C{:}NH\\ |\\ CCl\cdot NO_2\end{array}$ being formed as an intermediate product.

By means of these successive reactions, it has hence been found possible to pass from camphoroxime, or rather chlorocamphoroxime, which contains a nitrogen atom united to one of the carbon atoms, to chloronitrocamphor, in which a nitrogen atom is combined with the neighbouring carbon atom.

ψ-Chloropernitrosocamphor, to which the authors give the constitution $C_8H_{14}<\begin{array}{l}CH\cdot N\cdot O\\ |\quad\ \ |\quad |\\ CCl\cdot N\cdot O\end{array}$ or $C_8H_{14}<\begin{array}{l}CH\cdot N\text{--}\\ |\quad\ \ |\\ CCl\cdot NO\end{array}>O$, is readily acted on by potassium hydroxide solution, giving a *compound* which, when precipitated by acid, is obtained as a bluish-green substance; this soon becomes converted into a colourless and crystalline substance which melts at about 80°, is soluble in alkalis, and is probably a fourth isomeride.

For *iso*chloropernitrosocamphor, the author suggests the formula $C_8H_{14}<\begin{array}{l}C\text{---}N{:}O\\ \|\qquad \|\\ CCl\quad N\cdot OH\end{array}$ or $C_8H_{14}\langle\begin{array}{l}C\text{—}N\cdot O\\ \|\quad\ \ \vee\\ CCl\ \ N\cdot OH\end{array}$, and for chloropernitrosocamphor, $C_8H_{14}<\begin{array}{l}C{:}NO\cdot NO\\ |\\ CHCl\end{array}$. T. H. P.

Existence of Laurene. G. de Maria (*Gazzetta*, 1903, **33**, i, 407—412).—Doubts have been cast by several investigators on the existence of the compound $C_{11}H_{16}$, separated by Fittig, Köbrich, and Jilcke (*Annalen*, 1867, **145**, 129) from the products of the action of fused zinc chloride on camphor and termed by them laurene. Following the directions given by these authors, the present author has separated a hydrocarbon which has the composition $C_{10}H_{14}$ and seems to yield *p*-toluic acid when oxidised with nitric acid. These facts indicate that the hydrocarbon obtained by the author is either *p*-methyl-*n*- or *iso*-propylbenzene or a mixture of the two.

Besides the hydrocarbon, $C_{10}H_{14}$, carvacrol is also obtained by the action of fused zinc chloride on camphor. T. H. P.

Cyclic Compounds. Oxidation of Menthone, Pulegone, and β-Methylhexanone. Active and Racemic Pyrotartaric Acids and their Anhydrides. Wladimir B. Markownikoff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 226—253).—In the preparation of β-methyladipic acid by Manasse and Rupe's method (Abstr., 1894, i, 470), oxidation of menthone by means of permanganate, the author finds that only 50 to 70 per cent. of non-volatile acids are obtained, some 30—45 per cent. consisting of β-methyladipic acid and active pyrotartaric anhydride. The product of the oxidation contained also: *iso*butyrylmethylvaleric, β-acetopropionic, β-hydroxymethyladipic, γ-hydroxymethyladipic (?), methyl*iso*propyladipic (?), *iso*butyric, acetic, and propionic acids; those of the hydroxy-acids capable of yielding lactones were obtained in that form.

The β-methyladipic acid obtained melts at 90·5—91°, boils at 205° under 8 mm. and 230° under 30 mm. pressure, and has $[\alpha]_D$ +8·62°; its dianilide melts at 198—199°. On oxidising methyl-$\Delta^{2\cdot3}$-*cyclo*hexene by means of nitric acid, the same β-methyladipic acid is apparently obtained, but in this case two dianilides are formed, one melting at 197—198° and the other, less soluble in alcohol than the former, at 203—204·5°. If the methyl-$\Delta^{2\cdot3}$-*cyclo*hexene is oxidised by permanganate, it yields inactive β-methyladipic acid melting at 84·5—85·5°.

The *potassium, sodium, ammonium, barium, calcium, zinc, lead,* and *copper* salts of β-methyladipic acid were prepared and the last-named analysed.

Ethyl β-methyladipate, $C_7H_{10}O_4Et_2$, is a pleasant-smelling liquid boiling at 257° under 746 mm. pressure and having sp. gr. 1·0128 at 0°/0° and 0·9950 at 20°/0°.

Ethyl hydrogen β-methyladipate, $C_7H_{11}O_4Et$, boils at 164—166° and has sp. gr. 1·0830 at 0°/0° and 1·0673 at 20°/0°.

β-Methyladipic dianilide, $C_7H_{10}O_2(NHPh)_2$, is soluble in alcohol and generally melts at 197—198°, although occasionally it shows the melting point 201—203°.

β-Methyladipic monoanilide, $C_7H_{11}O_2{\cdot}NHPh$, is soluble in methyl or ethyl alcohol and in hot benzene or toluene, from which it separates in long, silky needles melting at 100—103°.

r-Pyrotartaric anhydride, $C_5H_6O_3$, separated from the products of oxidation of menthone, is readily soluble in alcohol, ethyl acetate, benzene, or acetone, and melts at 67—68°; it has $[\alpha]_D$ +3·8°.

The *r*-pyrotartaric acid, prepared from the anhydride, melts at 112·5—113·5° and gives the rotation α +47′ in 6·5 per cent. solution in a 200 mm. tube. These two compounds are probably admixed with the racemic compound, since Ladenburg gave higher values for the rotations of these substances. T. H. P.

Some Transformations of *d*-Pinene and Terpene Hydrate.

ANTONIO DENARO and GIUSEPPE SCARLATA (*Gazzetta*, 1903, **33**, i, 393—401).—The gradual and cautious addition of monochloroacetone and *d*-pinene to aluminium chloride at 0°, or the action of acetone on *d*-pinene in presence of aluminium chloride, gives rise to a colourless, oily *compound*, $C_{10}H_{16}O$, which has an odour of cloves and boils at 290°.

The action of sodium ethoxide on the tetra-iodo-derivative of pinene yields *tri-iodoethoxypinene*, $C_{10}H_{14}OI_3Et$, which is obtained as an oil; treatment with nascent hydrogen gives a fairly stable, oily *iodoethoxypinene*, $C_{10}H_{14}OIEt$, and an unstable *di-iodoethoxypinene*, $C_{10}H_{14}OI_2Et$.

An improved method for preparing terpinol consists in acting on terpene hydrate with aqueous zinc chloride and distilling with steam the liquid so obtained.

The action of hydriodic acid (2 mols.) on terpene hydrate and subsequent treatment with potassium hydroxide yields a compound, $C_8H_{12}O_4$, apparently identical with Hempel's terpenylic acid.

Chloroacetone and terpene hydrate yield terpinol and cajeputol.

T. H. P.

Phellandrene. Iwan L. Kondakoff (*J. pr. Chem.*, 1903, [ii], 68, 294—296. Compare Semmler, this vol., i, 641).—To test the correctness of Semmler's formulæ for phellandrene and ψ-phellandrene, the author proposes to attempt the conversion of the carvomenthene, obtained from *ter.*-carvomenthol, into phellandrene.

G. Y.

Ethereal Oil of Cassia Flowers. Heinrich Walbaum (*J. pr. Chem.*, 1903, [ii], 68, 235—250. Compare Abstr., 1901, i, 394).—The oil of cassia flowers (*Acacia Cavenia*) contains 40—50 per cent. of eugenol, 8 per cent. of methyl salicylate, and 52—42 per cent. of substances insoluble in dilute aqueous sodium hydroxide, consisting of benzyl alcohol (about 20 per cent.), geraniol, anisaldehyde, and eugenol methyl ether. Linalool, decylaldehyde, and a ketone with an odour of violets, ionone, or irone are probably present but could not be identified with certainty. The oil does not contain methyl anthranilate.

Anisaldehyde forms a *semicarbazone* which crystallises in white leaflets and melts at 203—204°.

The oil of cassia flowers (*Acacia Farnesiana*), obtained from Indian cassie pomade, contains benzaldehyde, salicylic acid, methyl salicylate, benzyl alcohol, an aldehyde, which has an odour resembling that of decylaldehyde and forms a semicarbazone melting at 97°, and a ketone, which has an odour of violets and forms a semicarbazone melting at 143°. Eugenol is not present.

A French specimen of oil of cassia flowers (*Acacia Farnesiana*), obtained by extraction with light petroleum, contains methyl salicylate and salicylic acid. The portion of the oil insoluble in aqueous sodium hydroxide has $[\alpha]_D + 0°50'$ and boils at 80—180°, the greater part at 90—115°, under 11 mm. pressure. The fraction boiling at 115—135° contains aldehydes and ketones, that boiling at 130° under 11 mm. pressure has an odour of violets.

G. Y.

Caoutchouc. III. Carl O. Weber (*Ber.*, 1903, 36, 3108—3115. Compare Abstr., 1902, i, 552).—The milk from *Castilloa elastica* has been investigated. When shaken with water at the ordinary temperature, it does not form a homogeneous emulsion, but on raising the temperature a liquid having the general appearance of mammalian milk is obtained. Although the milk contains as much as 7 per cent. of proteids, it does not coagulate to any appreciable extent when freed from caoutchouc and boiled; coagulation readily occurs, however, on the addition of a few drops of acetic acid. When the milk or the aqueous emulsion is kept for some time, it assumes a deep brown colour, and when subsequently warmed the whole of the proteids undergo coagulation. This change is probably due to the presence of an oxydase in the milk.

The statement that caoutchouc milk contains tannin is incorrect. The dark green coloration produced by iron salts is due to the presence of a glucoside, which, on hydrolysis, yields dambonitol (dimethyl-*l*-inositol).

Caoutchouc is insoluble in ether and does not exist as such in the

milk, since extraction of the milk with ether removes 28 per cent. of a viscid, oily constituent, which, after exposure to light, becomes solid and then possesses all the characteristics of caoutchouc. A *dry* ethereal solution of the oil can be kept for several weeks in a cool place without undergoing this transformation. The change (polymerisation ?) is brought about instantaneously by the addition of a little formic acid or hydrogen chloride.

In the india-rubber industry, this change is often accomplished by mechanical methods in the process of washing. J. J. S.

Quillajic Acid. Paul Hoffmann (*Ber.*, 1903, 36, 2722—2734).—Quillajic acid is one of the saponin group of glucosides. The author has prepared it from "*Saponinum depuratum*" according to Kobert's directions (Abstr., 1887, 55) and has found it to be identical with the product obtained from the extract of *Cortex quillajae.* The molecular weight, determined by the cryoscopic method, was 731·6, and the acid has the probable composition $C_{33}H_{52}O_{18}$ or $C_{33}H_{53}O_{18}$. It was obtained as a brown, amorphous, very hygroscopic powder; it is but faintly acid and does not expel carbon dioxide from carbonates. It is easily soluble in ethyl, *iso*butyl, and methyl alcohols and in water. By dilute acids, it is converted into sapogenin, galactose, and a dextrorotatory sugar which is not fermentable by yeast. Sapogenin, when acted on by dilute nitric acid, yields a nitro-derivative which softens at 197°. The nitro-derivative, formed when concentrated nitric acid is used, is explosive.

As by-products in the preparation of quillajic acid, were obtained acids melting at 167° and 207—208° respectively and a liquid boiling at 134—135° under 13 mm. pressure. A. McK.

Solanin. Albert Hilger and W. Merkens (*Ber.*, 1903, 36, 3204—3206).—Crude solanin is purified by extraction with boiling absolute alcohol and precipitation with acetic acid, water, and ammonia. Chlorophyll and colouring matters may be removed by ethyl acetate. The product is recrystallised from alcohol. Hydrolysis with 2 per cent. sulphuric acid forms crotonaldehyde, dextrose, and solanidine, according to the equation:

$$2C_{52}H_{97}O_{18}N = 2C_{39}H_{61}O_2N + 3C_6H_{12}O_6 + 2C_4H_6O + 12H_2O,$$

which was confirmed by analysis. Amorphous solanin (solanein) is an anhydride of crystalline solanin, being solanin $-5H_2O$. Acetone containing water converts amorphous into crystalline solanin in 8 months. C. H. D.

Some 1-Acylcoumarones and the Decomposition of 1-Acetylcoumarone. Richard Stoermer and M. Schäffer (*Ber.*, 1903, 36, 2863—2872. Compare Abstr., 1900, 650).—An improved method is given of preparing 1-acetylcoumarone from chloroacetone and the sodium derivative of salicylaldehyde, the yield being about 75 per cent. of the weight of aldehyde used.

1-*Dibromoacetylcoumarone*, $C_6H_4<\substack{O-\\CH}\geqslant C\cdot CO\cdot CHBr_2$, crystallises from chloroform in stout, white needles and melts at 90°, but could not be converted into the corresponding aldehyde by the action of water, lead oxide, or silver oxide. 2-*Acetyl-β-naphthafuran*,

$$C_{10}H_6<\substack{O-\\CH}\geqslant C\cdot CO\cdot CH_3,$$

prepared by condensing the sodium derivative of β-naphtholaldehyde with chloroacetone, crystallises from alcohol in large, scaly crystals and melts at 115—116°; the *semicarbazone*, $C_{15}H_{13}O_2N_3$, forms white, crystalline flocks and melts at 249°; the *phenylhydrazone*, $C_{20}H_{16}ON_2$, crystallises from alcohol in yellow, glistening scales and melts at 189°; the *oxime* forms minute needles and melts at 207°; the *bromo*-derivative, $C_{14}H_9O_2Br$, crystallises from chloroform and melts at 113°; the *dibromo*-derivative crystallises from chloroform in yellow, nodular masses and melts at 177°. *Coumarylketo-β-naphthafuran*,

$$C_{10}H_6<\substack{O-\\CH}\geqslant C\cdot CO\cdot C\leqslant\substack{O-\\CH}>C_6H_4,$$

prepared by condensing the monobromo-derivative with salicylaldehyde, crystallises from alcohol in stout, golden-yellow needles and melts at 200°.

1-*Aminoethylcoumarone*, $C_6H_4<\substack{O-\\CH}\geqslant C\cdot CHMe\cdot NH_2$, prepared by reducing acetylcoumaroneoxime, is a colourless oil which boils at 140° under 20 mm. pressure; the *hydrochloride* is a stable salt and melts at 114°; the *hydrobromide* is less stable and melts at 95°; the *hydriodide* is a somewhat unstable salt and melts at 144°; the *aurichloride* forms glistening, brown needles and melts at 117°; the *platinichloride* forms yellow flakes and melts at 191°; the *mercurichloride* crystallises from water in white needles and melts at 114°. 1-*Coumarylmethylcarbinol*, $C_6H_4<\substack{O-\\CH}\geqslant C\cdot CHMe\cdot OH$, prepared by the action of nitrous acid on the amine, boils at 145° under 15 mm. pressure and solidifies to a white, radiating, crystalline mass which melts at 37°; the *phenylurethane* melts at 126°. This compound is not formed on reducing acetylcoumarone with sodium; the first reduction product isolated is *coumaranylmethylcarbinol*, $C_6H_4<\substack{O-\\CH_2}>CH\cdot CHMe\cdot OH$, a colourless oil of powerful odour, which boils at 142° under 15 mm. pressure; the *phenylurethane* crystallises from dilute alcohol and melts at 73°. γ-o-*Hydroxyphenyl-α-methylpropyl alcohol*,

$$HO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CHMe\cdot OH,$$

a reduction product formed in rather larger quantities, is obtained as a colourless oil boiling at 188—192° under 15 mm. pressure, which solidifies to a white, radiating, crystalline mass, and when recrystallised from water separates in white needles and melts at 65°; the *monophenylurethane* crystallises from light petroleum in minute, white needles and melts at 90°; the *diurethane* forms white, nodular crystals and melts at 107·5°; by removal of a molecule of water, the

alcohol is converted into 2-methylchroman, $C_6H_4<\begin{matrix}O—CHMe\\CH_2\cdot CH_2\end{matrix}$.

T. M. L.

Synthesis of Coumaran and its Homologues. RICHARD STOERMER and FR. GÖHL (*Ber.*, 1903, **36**, 2873—2877).—Coumaran and its homologues can be prepared synthetically by the action of sodium on *o*-bromophenyl bromoethyl ethers, $C_6H_4Br\cdot O\cdot CH_2\cdot CH_2Br + 2Na = C_6H_4<\begin{matrix}O\\CH_2\end{matrix}>CH_2 + 2NaBr$.

o-*Chlorophenyl bromoethyl ether*, $C_6H_4Cl\cdot O\cdot CH_2\cdot CH_2Br$, is a colourless oil and boils at 140—142° under 13 mm. pressure. *Di*-o-*chlorophenyl ethylene ether*, $C_2H_4[O\cdot C_6H_4Cl]_2$, crystallises from alcohol in white flakes and melts at 103—104°. o-*Bromophenyl bromoethyl ether*, $C_6H_4Br\cdot O\cdot CH_2\cdot CH_2Br$, boils at 160—162° under 16 mm. pressure. *Di*-o-*bromophenyl ethylene ether*, $C_2H_4[O\cdot C_6H_4Br]_2$, crystallises from light petroleum in minute, white needles and melts at 110—111°. o-*Bromo*-p-*tolyl bromoethyl ether*, $C_6H_3MeBr\cdot O\cdot CH_2\cdot CH_2Br$, boils at 172—173° under 15 mm. pressure. *Di*-o-*bromo*-p-*tolyl ethylene ether*, $C_2H_4[O\cdot C_6H_3MeBr]_2$, crystallises from benzene in minute, white needles and melts at 156°. o-*Bromo*-m-*xylenyl bromoethyl ether*, $C_6H_2Me_2Br\cdot O\cdot CH_2\cdot CH_2Br$, boils at 172—173° under 13 mm. pressure. *Di*-o-*bromo*-m-*xylenyl ethylene ether*, $C_2H_4[O\cdot C_6H_2Me_2Br]_2$, separates from light petroleum in minute, white needles and melts at 100°.

4-*Methylcoumaran*, $C_6H_3Me<\begin{matrix}O\\CH_2\end{matrix}>CH_2$, prepared by the action of sodium on *o*-bromo-*p*-tolyl bromoethyl ether, boils at 210—211°, has a sp. gr. 1·042 at 19°, and n_D 1·5385 at 19°. 4 : 6-*Dimethylcoumaran*, $C_6H_2Me_2<\begin{matrix}O\\CH_2\end{matrix}>CH_2$, has a sp. gr. 1·029 at 19° and n_D 1·5340 at 19°.

T. M. L.

Compounds of Alkaloids with Hydroferrocyanic, Hydroferricyanic, Thiocyanic, and Nitroprussic Acids. MAURITS GRESHOFF (*Chem. Centr.*, 1903, ii, 385; from *Pharm. Weekblad*, **40**, 541—542).—Sparingly soluble precipitates are often obtained on mixing solutions of alkaloids with 10 per cent. solutions of sodium nitroprusside, potassium ferrocyanide, ferricyanide, or thiocyanate. The following were analysed:

Papaverine hydroferrocyanide, $C_{20}H_{21}O_4N,H_4Fe(CN)_6,5H_2O$. *Strychnine nitroprusside*, $(C_{21}H_{22}O_2N_2)_2,H_2FeNO(CN)_5$, crystallises from water. *Quinine nitroprusside*, $(C_{20}H_{24}O_2N_2)_2,H_2FeNO(CN)_5$, crystallises in bright brown needles from water or in garnet-red crystals from alcohol and decomposes at about 195°. *Quinidine nitroprusside*, $C_{20}H_{24}O_2N_2,H_2FeNO(CN)_5,2H_2O$, resembles the quinine derivative and decomposes at about 190°. W. A. D.

Oxidation Products of Codeine. FRITZ ACH and LUDWIG KNORR (*Ber.*, 1903, 36, 3067—3073).—Whilst the oxidation products of morphine throw no light on its constitution, the conditions are more favourable when codeine, the methyl ether of morphine, is oxidised.

When codeine is dissolved in sulphuric acid and then oxidised by chromic acid at 5—10°, the main product is *oxycodeine*, $C_{18}H_{21}O_4N$; it melts at 207—208°, gives a characteristic red coloration with concentrated sulphuric acid, and is easily soluble in dilute acids, from the solution of which it is precipitated in needles by sodium carbonate. The presence of two alcoholic groups in its molecule is indicated by the formation of a *diacetyl* derivative, which crystallises from alcohol in glistening prisms and melts at 160—161°. Oxycodeine is readily regenerated by the hydrolysis of the acetyl compound. Its *methiodide* crystallises from alcohol with $1\frac{1}{2}$EtOH. *Diacetyloxycodeine methiodide* separates in colourless crystals which decompose at 248—255°.

Codeineone, $C_{18}H_{19}O_3N$, is formed either by oxidising codeine with potassium permanganate in acetone solution or by using chromic acid in sulphuric acid solution and allowing the temperature to rise. Its relationship to codeine is that of ketone to alcohol. It separates from ethyl acetate in colourless prisms, which melt at 185—186° and assume a rose-coloured tint on exposure to air. It is more sparingly soluble in all solvents than codeine, and exhibits a stronger lævorotation, giving $[\alpha]_D$ $-205°$ at 15° ($c = 1·007$) in alcoholic solution. Its *hydrochloride* forms needles which part with their water of crystallisation at about 145° and then melt at 179—180°. The *picrate* decomposes at about 205°; the *picrolonate* crystallises from dilute alcohol in hexagonal prisms which decompose at about 228°. Codeineone exerts a disagreeable physiological effect on the skin. The *oxime* separates from alcohol in rectangular leaflets containing 1EtOH and melts and decomposes at 212°. From its solution in acid, it is reprecipitated by sodium carbonate. It gives $[\alpha]_D$ $-499°$ at 15° ($c = 0·1386$) in ethyl alcoholic solution. Its *methiodide* separates from water in tiny needles which contain $2H_2O$, and, when anhydrous, softens at 170° and melts completely at about 180°; it is very unstable. Codeineoneoxime can be reduced to codeine.

When nitrocodeine is further nitrated, a highly crystalline nitro-acid, $C_{16}H_{18}O_9N_2$, is formed. A. McK.

Morphine. IV. Conversion of Codeine into Thebenine, Morphothebaine, and Methylthebaol. LUDWIG KNORR (*Ber.*, 1903, 36, 3074—3083).—The following conclusions are drawn respecting the constitution of morphine. Morphine is a derivative of 3 : 4 : 6-trihydroxyphenanthrene. The oxygen atom in position 4 is an indifferent "bridge oxygen" atom, the hydroxyl in position 3 is phenolic, and the hydroxyl in position 6 is alcoholic. Thebaine is the methyl ether of the enolic form of codeineone. In the morphol formation, the alcoholic hydroxyl of morphine and not the indifferent oxygen atom is attacked. The methoxyl grouping in thebaine, which suffers hydrolysis to a phenolic hydroxyl grouping, is in position 6. Thebaine or codeineone, when boiled with acetic anhydride, forms a hydramine and a phenanthrene derivative, the former containing one hydroxyl grouping and

the latter three. The nitrogen atom in morphine is in position 5 of the phenanthrene ring. The formula for morphine, suggested by Pschorr, Jaeckel and Fecht (this vol., i, 193), does not satisfactorily account for the splitting off of hydramine and for the formation of pyrene from thebenol and thebenine.

When codeineone is boiled with acetic anhydride, it forms a diacetoxymethoxyphenanthrene, which melts at 162—163°. The acetyl groups in this compound can be replaced by methyl groups and the resulting yellow oil yields a picrate which, when crystallised from alcohol, melts at 107—109° and is identical with methylthebaol picrate (Pschorr, Seydel, and Stöhrer, this vol., i, 167; Vongerichten, this vol., i, 168). From the mother liquor remaining after removal of the diacetoxymethoxyphenanthrene, the hydramine (ethanolmethylamine) was isolated in the form of its gold salt, which was identical with the product obtained from thebaine.

When codeineone is boiled for a few minutes with dilute hydrochloric acid, thebenine hydrochloride, $C_{18}H_{19}O_3N,HCl$, is formed; it melts at 235°. When codeineone is decomposed by a methyl alcoholic solution of hydrogen chloride, methebenine hydrochloride, crystallising at 245°, is produced. Codeineone is converted into morphothebaine hydrochloride by being heated in a sealed tube at 100° with fuming hydrochloric acid; this hydrochloride melts at 158° and is identical with the product obtained by Freund (Abstr., 1899, i, 307) from thebaine. The base melts and decomposes at about 197°.

A. McK.

Constitution of *d*-Lupanine from Lupinus Albus. ARTURO SOLDAINI (*Gazzetta*, 1903, 33, i, 428—440).—The oxidation of *d*-lupanine yields products varying very considerably with the conditions of temperature, dilution, &c., under which the oxidation is carried out. From the results obtained, the author concludes that *d*-lupanine probably contains an ethylene or oxy-ethylene grouping which, in certain conditions, is oxidised and eliminated as oxalic acid. T. H. P.

Piperidyl-2-acetic Acid and Condensation of γ-Picoline [4-Methylpyridine] and of 2:6-Dimethylpyridine with Formaldehyde. WILHELM KOENIGS and GUSTAV HAPPE (*Ber.*, 1903, 36, 2904—2912. Compare Abstr., 1902, i, 394).—Piperidyl-2-acetic acid is not readily oxidised; it forms an aurichloride which crystallises in yellow needles melting and decomposing at 171—172°.

2:6-Dimethylpyridine is best isolated from commercial 2-picoline by conversion into its *ferrocyanide*, which is then decomposed by alkali. Its hydrochloride melts at 230°, decomposes at a somewhat higher temperature, and when pure is not hygroscopic (compare Ladenburg, Abstr., 1888, 498).

When heated with 35 per cent. formaldehyde solution for 10 hours at 135—140°, the base is converted into 2-methyl-6-hydroxyethylpyridine. The platinichloride melts and decomposes at 196—198°, and the aurichloride melts at 153—155°. The hydrochloride, mercurichloride, and picrate have not been obtained in a crystalline form. On oxidation it yields 2-methylpyridine-6-carboxylic acid (Ladenburg and Scholtze

Abstr., 1900, i, 409) which, after recrystallisation from benzene, melts at 128—129°.

The mixture of 2- and 4-picolines, left after the removal of the lutidine from commercial β-picoline, reacts with formaldehyde solution at 100°, yielding *4-pyridyl*-ter.-*butantriol* (*trimethylol*-4-*picoline*), $C_5NH_4\cdot C(CH_2\cdot OH)_3$, which crystallises from alcohol in colourless needles melting at 156—157°, although it begins to turn pink at 100°. The *hydrochloride* melts at 137—138° and is very readily soluble in water.

By the action of hydriodic acid and phosphorus at 150—160°, it is transformed into the *tri-iodohydrin*, $C_5NH_4\cdot C(CH_2I)_3$, melting at 136° and insoluble in water. The iodine derivative, on reduction with hydriodic acid and zinc dust, yields 4-ter.-*butylpyridine*, $C_5NH_4\cdot CMe_3$, which boils at 196—197° and has a characteristic odour. Its *aurichloride* melts at 184°; the *platinichloride* is somewhat more soluble and melts and decomposes at 212—213°.

*iso*Nicotinic acid is obtained when the trihydroxy-derivative is oxidised with nitric acid. J. J. S.

Additive Products of Quinone with Salts of Pyridine and Quinoline. Giovanni Ortoleva (*Gazzetta*, 1903, 33, i, 164—168. Compare Abstr., 1902, i, 54 and 674).—By adding a slight excess of concentrated hydrofluoric acid solution to a mixture of quinone and pyridine, the *additive* compound, $C_6H_4O_2,C_5H_5N,3HF$, is obtained; it crystallises from water in yellow scales melting and decomposing at 240—242°, and is slightly soluble in alcohol. It has a strongly acid reaction in aqueous solution and dissolves in alkali hydroxides, giving a red coloration, whilst alcoholic potassium hydroxide dissolves it, forming a violet liquid. By the addition of hydrochloric acid to its solutions in alkali hydroxides, the corresponding additive product of quinone and pyridine hydrochloride, melting at 223—225°, is obtained (*loc. cit.*).

The *additive product*, $C_6H_4O_2,C_5H_5N,HNO_3$, prepared from quinone, pyridine, and dilute nitric acid, separates from water in yellow needles melting at 212—214° and dissolves in alkalis with formation of a red coloration.

The *additive product*, $C_6H_4O_2,C_9H_7N,HI$, obtained either by adding iodine to an alcoholic solution of quinol and quinoline or by adding hydriodic acid to a mixture of quinone and quinoline, crystallises from water in yellow needles containing $1H_2O$ and melting at 223—225°; it is readily soluble in alcohol and is dissolved also by aqueous alkali hydroxides giving a red coloration, and by alcoholic potassium hydroxide, to which it imparts a green coloration, gradually changing to reddish-brown.

The *additive product* of quinone with quinoline hydrochloride, $C_6H_4O_2,C_9H_7N,HCl$, prepared by the action of concentrated hydrochloric acid on the corresponding hydriodide (see above), crystallises in yellow needles melting at 144—146°; it is soluble in alkali solution giving a red coloration, and in alcoholic potassium hydroxide yielding a greenish-blue solution.

These results, together with those previously obtained by the author

(*loc. cit.*), show that additive products with pyridine and quinoline salts are only obtained with *o*- and *p*-benzoquinones. T. H. P.

Behaviour of Ethyl 3 : 5-Dimethyldihydropyridine-2 : 6-dicarboxylate at High Temperatures and in presence of Spongy Palladium. EMIL KNOEVENAGEL and JULIUS FUCHS (*Ber.*, 1903, **36**, 2848—2857).—The amount of hydrogen liberated from 2 grams of ethyl 3 : 5-dimethyldihydropyridine-2 : 6-dicarboxylate when heated for 1 hour with 0·1 gram of spongy palladium increased gradually from 101 c.c. at 180—185° to 145 c.c. at 305—310°, the maximum quantity theoretically possible, according to the equation

$$C_5NH_3Me_2(CO_2Et)_2 = H_2 + C_5NHMe_2(CO_2Et)_2,$$

being 175·4 c.c. ; when diluted with twice its weight of toluene, 19 c.c. were liberated at 115—120°, and liberation of gas can be detected even at 85—90°. Similar results were obtained with 0·02 gram of palladium, and although the amounts of hydrogen liberated were somewhat greater, in no case was the theoretical maximum reached. Experiments were therefore made in which the action was continued until no more gas was liberated, and it was found that after 8 hours' heating at 305—310°, 171 out of 175 c.c. were liberated, but that at lower temperatures the volume of gas was much less, although the ester was completely decomposed ; an examination of the solid residue showed that a considerable amount of the hexahydro-ester had been produced.

The unimolecular character of the decomposition was shown in an experiment in which 1 gram of the dihydro-ester was heated at 263° with 9 grams of ethyl 3 : 5-dimethylpyridine-2 : 6-dicarboxylate ; after the first 19 minutes, the velocity constant was quite steady. At temperatures above 300°, a further decomposition takes place, one of the carbethoxy-groups is eliminated with separation of carbon dioxide and ethylene, and ethyl 3 : 5-dimethylpyridine-2-carboxylate is obtained.

T. M. L.

Constitution of Apophyllenic Acid. ALFRED KIRPAL (*Monatsh.*, 1903, **24**, 519—525. Compare Kirpal, Abstr., 1902, i, 564 ; this vol., i, 117 ; Kaas, this vol., i, 117).—Apophyllenic acid, which was formerly considered to be methylbetaine-3-carboxy*iso*nicotinic acid, is now shown to be nicotinicmethylbetaine-4-carboxylic acid,

$$\begin{array}{lcl} CH\colon CH\cdot NMe & \text{———} & O \\ | \qquad\quad > CH & & | \\ C(CO_2H)\colon C & \text{———} & CO \end{array} .$$

Methyl apophyllenate, prepared from methyl iodide and silver apophyllenate, melts and decomposes at 218° and is identical with 4-methyl methylbetainecinchomeronate. The fact that the latter compound may be prepared by interaction of methyl iodide and 4-methyl cinchomeronate, which form an additive compound from which hydrogen iodide is eliminated, is adduced as evidence for the constitution of apophyllenic acid. Further, methyl iodide interacts with 3-methyl cinchomeronate to form an additive compound, which then yields a

betaine ester with properties differing from those of the betaine ester obtained from apophyllenic acid. 3-Methyl methylbetainecinchomeronate contains $1H_2O$, forms colourless needles, and melts and decomposes at 182°; when hydrolysed with dilute hydrochloric acid, potassium hydroxide, or silver oxide, it forms apophyllenic acid. The non-formation of an isomeric apophyllenic acid thus shows that, of the two possible betaines of cinchomeronic acid, the one is incapable of existing in the free state, whilst apophyllenic acid is very stable.

When 3-methyl cinchomeronate is heated at 154°, it undergoes rearrangement into apophyllenic acid, a small amount of 4-methyl cinchomeronate being simultaneously formed. Similarly, methyl *iso*nicotinate is transformed into methylbetaine-*iso*nicotinic acid.

A method for preparing apophyllenic acid by the action of nitric acid on cotarnine is described. A. McK.

Formation of 3-Pyridine Derivatives by Ladenburg's Reaction. Alexei E. Tschitschibabin (*Ber.*, 1903, 36, 2709—2711).—By the action of benzyl chloride or iodide on pyridine, the author had previously prepared 2- and 4-benzylpyridines (Abstr., 1901, i, 484). The mixture of bases, obtained as a by-product, was oxidised by potassium permanganate and sulphuric acid and a considerable quantity of pyridine-2-carboxylic acid was isolated, whilst only a small amount of pyridine-3-carboxylic acid was obtained. By the action of alkyl haloids, therefore, on pyridine at elevated temperature, there is formed, in addition to the 2- and 4-isomerides discovered by Ladenburg, a small amount of the 3-isomeride. 3-Ethylpyridine is also produced in small amount when ethyl iodide acts on pyridine. A. McK.

3-Benzylpyridine and its Derivatives. Alexei E. Tschitschibabin (*Ber.*, 1903, 36, 2711—2713. Compare preceding abstract).—3-Benzoylpyridine melts at 42° and boils at 319° (corr.) under 741 mm. pressure. When reduced by hydriodic acid and red phosphorus, it forms 3-*benzylpyridine*, which crystallises in needles, melts at 34°, boils at 286—287° under 740 mm. pressure, and is very soluble in alcohol and ether and almost insoluble in water; its *platinichloride* melts and decomposes at 200—202°, whilst its *picrate* melts at 126—127°. When reduced by sodium, according to the Wischnegradsky-Ladenburg method, it forms 3-*benzylpiperidine*, a syrupy liquid, which boils at 278—279° and is insoluble in water but miscible in all proportions with alcohol and with ether; it is a strong base, forming salts which crystallise with difficulty; its *platinichloride* melts and decomposes at 191—192°. A. McK.

Indolinone. H. Schwarz (*Monatsh.*, 1903, 24, 568—578. Compare Brunner, Abstr., 1897, i, 100; 1898, i, 90).—*β-Methylbutyrylphenylhydrazide* separates from dilute aqueous alcohol in colourless leaflets and melts at 104°. When heated with calcium oxide for two hours at 227° in a current of hydrogen and the product treated with concentrated hydrochloric acid, 3-iso*propylindolinone*,

$C_6H_4<\underset{N}{\overset{CHPr^\beta}{}}\geqslant C\cdot OH$, is formed; it crystallises in needles, melts at 106°, and gives the colour reactions characteristic of indolinones. Its *silver* derivative melts at 163°. Its *methyl ether*, prepared by the action of methyl iodide on the silver derivative, is of the lactim type and separates from ether in pyramids melting at 82°; it is converted into the original indolinone by means of hydrogen iodide. The corresponding *lactam methyl ether*, prepared by heating 3-*iso*propylindolinone with sodium methoxide, methyl alcohol, and methyl iodide at 110—120° for 16 hours, separates from alcohol in white needles which melt at 96°. *Acetyl*-3-iso*propylindolinone* separates from alcohol in greenish-white prisms and melts at 104°.

Dibromo-3-iso*propylindolinone*, $C_6H_2Br_2<\underset{N}{\overset{CHPr^\beta}{}}\geqslant C\cdot OH$, prepared by the action of bromine water on a solution of 3-*iso*propylindolinone in dilute sulphuric acid, separates from alcohol as a yellowish-brown, crystalline powder and melts at 142°.

β-Methylbutyrylphenylmethylhydrazide, prepared by heating phenylmethylhydrazine with β-methylbutyric acid at 140° for 3—4 hours, separates from alcohol in white leaflets and melts at 61°. When heated with calcium oxide, it yields 3-*iso*propylindolinone lactam methyl ether. A. McK.

Derivatives of Indandione [Diketohydrindene]. Synthesis of α-Diorthobenzylenepyridine. GIORGIO ERRERA (*Gazzetta*, 1903, 33, i, 417—428. Compare this vol., i, 265).—*Hydroxymethyleneindandione*, $C_6H_4<\substack{CO\\CO}>C:CH\cdot OH$, prepared by the condensation of indandione with ethyl orthoformate in presence of acetic acid, separates from the solution, on adding a little water or on being left exposed to the air, in red needles or plates containing $1H_2O$; it melts at 141—142°, and in solution in water or alcohol rapidly changes into methyl*bis*indandione (see later), to which is due the red colour, since when crystallised from benzene it is obtained colourless but still hydrated; it is a strong acid, turning litmus red and decomposing carbonates in the cold. The *sodium* derivative separates from water in yellow needles slightly soluble in alcohol; the *ammonium* compound forms yellow needles and, on heating, readily loses water, yielding aminomethyleneindandione (see later); the *copper* derivative, $(C_{10}H_5O_3)_2Cu$, is a yellow powder insoluble in water, and the *silver* compound is deposited from aqueous solution in long, yellow needles.

Aminomethyleneindandione, $C_6H_4<\substack{CO\\CO}>C:CH\cdot NH_2$, prepared as first described or by the action of ammonia on methenyl*bis*indandione, separates from alcohol or benzene in yellow needles or from ethyl acetate in hard, lustrous crystals which melt and decompose at 240°; it dissolves in alkali hydroxide solution yielding ammonia and the corresponding salt of hydroxymethyleneindandione.

*Methenyl*bis*indandione*, $C_6H_4<\substack{CO\\CO}>C:CH\cdot CH<\substack{CO\\CO}>C_6H_4$, formed as previously mentioned or, together with anhydrodiketohydrindene, by

the action of indandione on hydroxymethyleneindandione, crystallises from xylene in long, red needles melting at 303°; it is slightly soluble in alcohol or benzene and more so in acetic acid, yielding intensely coloured solutions; it has acid properties, and its alkaline salts are orange-yellow and but slightly soluble in water; when treated with hydroxylamine, it yields various products to be described later; with aqueous ammonia, it gives, on the one hand, indandione and amino-methyleneindandione, and on the other, by a cyclic condensation, a *diorthobenzylenonepyridine* (*a-diphenylenepyridine diketone*),

$$\begin{array}{l}\mathrm{CH\cdot CH{:}C\cdot CO\cdot C\cdot CH{:}C\cdot CO\cdot C{:}CH\cdot CH}\\ \mathrm{CH\cdot CH{:}C\text{——}C\cdot N{=}C\text{——}C{:}CH\cdot CH}\end{array}$$

which separates from pyridine solution in golden-yellow needles changing, in contact with the mother liquor, into short, yellowish-brown prisms melting at 256°; its *dioxime*, $C_{19}H_{11}O_2N_3$, is obtained as a yellow powder which is insoluble in the ordinary solvents, but soluble in bases, and decomposes on heating.

a-Diorthobenzylenolpyridine,

$$\begin{array}{l}\mathrm{CH\cdot CH{:}C\cdot CH(OH)\cdot C\cdot CH{:}C\cdot CH(OH)\cdot C{:}CH\cdot CH}\\ \mathrm{CH\cdot CH{:}C\text{————}C\cdot N{=}C\text{————}C{:}CH\cdot CH}\end{array}$$

prepared by boiling an acetic acid solution of the preceding compound with zinc dust, separates from alcoholic solution in pale yellow needles, soluble in acetic acid and melting at 270—275°; in dilute acetic acid solution, it presents a beautiful violet fluorescence.

a-Di-o-benzylenepyridine, $\begin{array}{l}\mathrm{CH\cdot CH{:}C\cdot CH_2\cdot C\cdot CH{:}C\cdot CH_2\cdot C{:}CH\cdot CH}\\ \mathrm{CH\cdot CH{:}C\text{——}C\cdot N{=}C\text{——}C{:}CH\cdot CH}\end{array}$,

prepared by the reduction of the preceding compound by means of hydriodic acid and phosphorus, crystallises from benzene in pale yellow needles, slightly soluble in alcohol and more so in pyridine; it melts at 205° and distils unchanged at a high temperature; it is a weak base, and gives salts insoluble in all the ordinary solvents; it dissolves in hot concentrated sulphuric acid, which, on cooling, deposits the *sulphate* in crystalline plates; the *hydrochloride* separates from alcohol in slender needles; the hydriodide gives an additive product with iodine; the *picrate*, $C_{25}H_{16}O_7N_4$, crystallises in yellow plates which soften and decompose at about 260°. T. H. P.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. I. RUDOLF ANDREASCH and ARTUR ZIPSER (*Monatsh.*, 1903, 24, 499—518).—The condensation products of rhodanic acid with aldehydes are dyes which are of no practical applicability (Zipser, this vol., i, 273). In order to obtain more stable dyes, the condensation products of *N*-substituted rhodanic acids with aldehydes have now been prepared.

3-Phenylrhodanic acid, $CH_2<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{S—CS}\end{matrix}$, prepared by heating an aqueous alcoholic solution of phenylthiocarbimide with thioglycollic acid in a current of hydrogen, crystallises from alcohol in leaflets or needles and melts at 192—193° (von Braun, this vol., i, 13, gives 188°). When acted on by alkali, it forms a substance which separates

from light petroleum in colourless needles melting at 150°, the constitution of which has not yet been determined.

3-*Allylrhodanic acid*, $\mathrm{CH_2}<\begin{matrix}\mathrm{CO\cdot N\cdot C_3H_5}\\ \mathrm{S-CS}\end{matrix}$, prepared from allylthiocarbimide and thioglycollic acid, is a yellow oil insoluble in water.

3-*Phenyl*-5-*benzylidenerhodanic acid*, $\mathrm{CHPh{:}C}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{S-CS}\end{matrix}$, best prepared by heating molecular quantities of benzaldehyde and 3-phenylrhodanic acid with anhydrous sodium acetate and acetic acid and then crystallising the product from alcohol (the method used for the preparation of most of the other condensation products described), separates in yellow needles and melts at 186°.

5-*Benzylidene*-3-*allylrhodanic acid* separates in yellow leaflets or needles and melts at 144°. When it is boiled with excess of baryta water, allylamine is evolved and thiolcinnamic acid is produced, thus, $\mathrm{C_{13}H_{11}ONS_2 + 3H_2O = CHPh{:}C(SH)\cdot CO_2H + C_3H_5\cdot NH_2 + H_2S + CO_2}$.

5-o-*Hydroxybenzylidene-3-allylrhodanic acid*,

$$\mathrm{OH\cdot C_6H_4\cdot CH{:}C}<\begin{matrix}\mathrm{CO\cdot N\cdot C_3H_5}\\ \mathrm{S-CS}\end{matrix},$$

prepared by the addition of sodium hydroxide solution to an alcoholic solution of salicylaldehyde and allylrhodanic acid, melts at 179° and dissolves in aqueous alkalis to a red solution, from which it can be precipitated by addition of acid.

3-*Phenyl*-5-p-*methoxybenzylidenerhodanic acid*,

$$\mathrm{OMe\cdot C_6H_4\cdot CH{:}C}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{S-CS}\end{matrix},$$

prepared from anisaldehyde and phenylrhodanic acid, forms yellow needles and melts at 221°.

5-p-*Methoxybenzylidene-3-allylrhodanic acid* forms yellow needles and melts at 114°.

3-*Phenyl*-5-*methylenedioxybenzylidenerhodanic acid*,

$$\mathrm{CH_2{:}O_2{:}C_6H_3\cdot CH{:}C}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{S-CS}\end{matrix},$$

prepared from piperonal and 3-phenylrhodanic acid, forms yellow needles and melts at 193°.

5-*Methylenedioxybenzylidene*-3-*allylrhodanic acid* forms yellow needles and melts at 151°.

3-*Phenyl*-5-o-*nitrobenzylidenerhodanic acid*,

$$\mathrm{NO_2\cdot C_6H_4\cdot CH{:}C}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{S-CS}\end{matrix},$$

prepared from *o*-nitrobenzaldehyde and 3-phenylrhodanic acid, forms orange-red plates and melts at 238°.

5-o-*Nitrobenzylidene*-3-*allylrhodanic acid* melts at 73°.

3-*Phenyl-5-cinnamylidenerhodanic acid*, $\mathrm{CHPh{:}CH\cdot CH{:}C}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{S-CS}\end{matrix}$, prepared from cinnamaldehyde and 3-phenylrhodanic acid, forms orange-red needles and melts at 217°.

5-*Cinnamylidene-3-allylrhodanic acid* forms gold-coloured scales and melts at 166°.

5-p-*Methoxybenzylidenerhodanic acid*, $OMe\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NH\\ S-CS\end{matrix}$, prepared from anisaldehyde and rhodanic acid, forms golden needles which melt and decompose at 130—142°.

5-*Methylenedioxybenzylidenerhodanic acid*,

$$CH_2:O_2:C_6H_3\cdot CH:C<\begin{matrix}CO\cdot NH\\ S-CS\end{matrix},$$

prepared from piperonal and rhodanic acid, forms microscopic needles which begin to decompose at 245°.

5-o-*Hydroxybenzylidenediphenylthiohydantoin*,

$$HO\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\cdot NPh\\ S-C:NPh\end{matrix},$$

prepared from salicylaldehyde and diphenylthiohydantoin, forms bright yellow needles and melts at 230—235°.

5-*Methylenedioxybenzylidenediphenylthiohydantoin*, prepared from piperonal and diphenylthiohydantoin, melts at 160°. A. McK.

Chlorination of 4-Amino- and 4-Hydroxy-2′ : 4′-Dinitrodiphenylamine. Frédéric Reverdin and Pierre Crépieux (*Arch. Sci. phys. nat.*, 1903, [iv], 16, 257—272).—When 2′ : 4′-dinitro-4-aminodiphenylamine is treated with sodium chlorate in presence of hydrochloric acid, the amino-group undergoes oxidation, and chloro-derivatives of 2′ : 4′-dinitro-4-hydroxydiphenylamine are obtained.

3 : 5-*Dichloro-2′ : 4′-dinitro-4-hydroxydiphenylamine*, so prepared, crystallises in orange-red needles, melts at 207°, is soluble in alcohol and ether, but insoluble in light petroleum. The *sodium* derivative forms brilliant black needles and the *acetyl* derivative citron-yellow crystals melting at 207—208°. The constitution of this dichloro-compound was established from its synthesis by the condensation of chloro-2 : 4-dinitrobenzene with 2 : 6-dichloro-4-aminophenol.

3 : 5-*Dichloroquinone-2′ : 4′-dinitrophenylimide*,

$$O:C_6H_2Cl_2:N\cdot C_6H_3(NO_2)_2,$$

produced by the further action of sodium chlorate and hydrochloric acid on the foregoing or by the more vigorous action of the same reagent on the parent substance, crystallises in orange-yellow needles, melts at 219—220°, is slightly soluble in alcohol and ether, readily so in acetone and benzene. It reacts with aniline to form a *product* which crystallises in slender needles, and with ammonia to form a *substance* soluble in solution of sodium carbonate. It is readily reduced by sulphurous acid to the corresponding phenol already described, and when boiled with an aqueous solution of sodium carbonate is slowly converted into the sodium derivative of this. A similar change is brought about by strong sulphuric acid, accompanied, however, by fission of the molecule with the formation of 3 : 5-dichloroquinone and 2 : 4-dinitroaniline.

Trichloroquinone-2′ : 4′-dinitrophenylimide, produced by the action of a large excess of the chlorinating mixture on 4-amino-2′ : 4′-dinitrodiphenylamine, crystallises in orange-red needles, melts at 216°, is slightly soluble in alcohol, and insoluble in light petroleum or in sodium carbonate solution.

2′ : 4′-Dinitro-4-acetoxydiphenylamine melts at 137° (compare Nietzki and Simon, Abstr., 1896, i, 164), and when treated with sodium chlorate and hydrochloric acid furnishes 2-*chloro*-2′ : 4′-*dinitro*-4 *acetoxydiphenylamine*, which crystallises in lemon-yellow needles, melts at 170°, and is slightly soluble in cold alcohol, more so on warming. 2-*Chloro*-2′ : 4′-*dinitro*-4-*hydroxydiphenylamine*, produced by hydrolysis of the foregoing, or by condensation of 3-chloro-4-aminophenol with 1-chloro-2 : 4-dinitrobenzene, crystallises in red, prismatic needles and melts at 189°. On further chlorination, it furnishes an orange-red *substance*, which melts at 211° and may be either the 2 : 3 : 5- or 2 : 3 : 6-trichloroquinone-2′ : 4′-dinitrophenylimide, since when decomposed by dilute sulphuric acid it furnishes 2 : 4-dinitroaniline and trichloroquinone. When warmed with an aqueous solution of sodium carbonate, it is converted into the *sodium* derivative of the corresponding *phenol*. The latter is orange-red and melts at about 211°; its *acetyl* derivative forms lemon-yellow prisms and melts at 153°. 2-Chloro-2′ : 4′-dinitro-4-hydroxydiphenylamine closely resembles the isomeride obtained by condensing 1-chloro-2 : 4-dinitrobenzene with 2-chloro-4-aminophenol (D.R.-P., 1900, 128725), but the latter melts at 183°, furnishes an orange-yellow acetyl derivative which sinters at 149° and is completely melted at 156°, and yields 3 : 5-dichloroquinone-2′ : 4′-dinitrophenylimide on treatment with sodium chlorate and hydrochloric acid.

2-*Bromo*-2′ : 4′-*dinitro*-4-*acetoxydiphenylamine*, obtained by brominating 2′ : 4′-dinitro-4-acetoxydiphenylamine, dissolved in acetic acid, crystallises in slender, yellow needles and melts at 165—166°. The corresponding *hydroxy*-compound forms red crystals, melts at 178—179°, and possesses properties similar to those of the analogous chloro-derivative.

When 2′ : 4′-dinitro-4-acetylaminodiphenylamine is treated with sodium chlorate and hydrochloric acid, a *product* is obtained which melts at 163° and is difficult to purify.

Dichloro-2′ : 4′-*dinitro*-2-*ethoxydiphenylamine*, obtained by chlorinating 2′ : 4′-dinitro-2-ethoxydiphenylamine, forms orange-red needles, melts at 185—186°, is soluble in acetone, and sparingly so in alcohol. The analogous *methoxy*-compound forms red needles and melts at 206—207°.

2′ : 4′-Dinitro-4-ethoxydiphenylamine and the analogous methoxy-compound, when chlorinated, furnish 3 : 5-dichloroquinone-2′ : 4′-dinitrophenylimide already described.

Dichloro α-naphthyl-2′ : 4′-*dinitrophenylamine*, obtained similarly, crystallises in sulphur-yellow needles and melts at 179°. *Chloro-β-naphthyl*-2′ : 4′-*dinitrophenylamine* crystallises in orange-yellow leaflets, melts at 206°, and is sparingly soluble in ether or alcohol, more so in benzene or acetone. There is formed with this a *product* of uncertain composition, which is readily soluble in acetic acid and decomposes at 166—172° with the evolution of hydrogen chloride.

T. A. H.

Molecular Rearrangement of Unsymmetrical Acylamidines into Isomeric Symmetrical Derivatives. HENRY L. WHEELER, TREAT B. JOHNSON, and DAVID F. MCFARLAND (*J. Amer. Chem. Soc.*,

1903, 25, 787—798).—as-*Benzoylphenylbenzenylamidine*,

$NH\colon CPh\cdot NPhBz$,

prepared by the action of benzoyl chloride on phenylbenzenylamidine, is a crystalline substance which melts at 95—97° and, when treated with dilute hydrochloric acid, undergoes hydrolysis with the formation of benzanilide and benzamide. If left for some time or if warmed with alcohol, it undergoes a molecular rearrangement with production of *s*-benzoylphenylbenzenylamidine.

When phenylbenzenylamidine is treated with acetyl chloride, a mixture of *as-* and *s*-acetylphenylbenzenylamidines is obtained. as-*Acetylphenylbenzenylamidine*, $NH\colon CPh\cdot NPhAc$, crystallises from alcohol in colourless prisms, melts at 128—129°, and, on hydrolysis with hydrochloric acid, yields acetanilide. Unlike the corresponding benzoyl derivative, it shows no tendency to undergo molecular rearrangement, even at a temperature of 150—160°.

By the action of benzoyl chloride on phenyl-phenylethenylamidine, $CH_2Ph\cdot C(NPh)\cdot NH_2$, benzoylphenylacetamide, benzanilide, and *as*-benzoylphenyl-phenylethenylamidine are produced. *Benzoylphenylacetamide*, $CH_2Ph\cdot CO\cdot NHBz$, crystallises in colourless prisms and melts at 129—130°. as-*Benzoylphenyl-phenylethenylamidine* crystallises from alcohol in colourless plates, melts at 110—111°, and when treated with hydrochloric acid yields benzanilide; it shows no tendency to undergo a molecular rearrangement. *Dibenzoylphenylphenylethenylamidine*, formed by the action of benzoyl chloride on phenyl-phenylethenylamidine in presence of pyridine, crystallises in colourless prisms, melts at 175°, and when treated with hydrochloric acid is converted into a mixture of benzanilide, phenylacetamide, and benzoic acid.

When phenyl-*p*-tolenylamidine is treated with benzoyl chloride, a mixture of the two isomeric benzoyl derivatives is produced. The *as*-compound readily suffers a molecular rearrangement with the formation of the *s*-derivative. s-*Benzoylphenyl*-p-*tolenylamidine* crystallises from alcohol in colourless prisms, melts at 126°, and by the action of hydrochloric acid is converted into p-*toluoylbenzamide*,

$C_6H_4Me\cdot CO\cdot NHBz$,

which crystallises in colourless needles and melts at 112—113°.

By the action of benzoyl chloride on *o*-tolylbenzenylamidine, dibenzoyl-*o*-tolylbenzenylamidine and *s*-benzoyl-*o*-tolylbenzenylamidine are produced; the formation of the *as*-derivative was not observed. s-*Benzoyl*-o-*tolylbenzenylamidine* crystallises from alcohol in colourless prisms, melts at 111—113°, and by the action of hydrochloric acid is converted into dibenzamide.

o-*Phenylguanidinebenzoic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot C(NH)\cdot NHPh$, formed by the action of *o*-aminobenzoic acid on phenyl-ψ-methylthiocarbamide, crystallises from alcohol in colourless prisms and melts at 248°. If left in contact with a solution of sodium hydroxide or hydrochloric acid, it is converted into 2-*phenylamino*-4-*ketodihydroquinazoline*, $C_6H_4\!<\!\begin{matrix} N{=}C\cdot NHPh \\ CO\cdot NH \end{matrix}$, which crystallises from alcohol in slender needles and melts at 256°.

2-Chloro-3-phenyl-4-ketodihydroquinazoline (McCoy, Abstr., 1897, i, 491) forms colourless prisms and melts at 132°. When this compound is heated in a closed tube at 120—130° with alcoholic ammonia, *2-amino-3-phenyl-4-ketodihydroquinazoline*,

$$C_6H_4<\begin{matrix}N{=}C\cdot NH_2\\ CO\cdot NPh\end{matrix},$$

is produced, which crystallises from alcohol in colourless prisms, melts at 237—238°, and when boiled with dilute hydrochloric acid is converted into 3-phenyl-2 : 4-diketotetrahydroquinazoline ; it does not undergo a molecular rearrangement when heated above its melting point. E. G.

[Dialkylaminohydroxydiphenylamines.] LEOPOLD CASSELLA & Co. (D.R.-P. 140733).—p-*Dimethylaminophenyl*-p-*hydroxy*-m-*tolylamine*, prepared by heating amino-*o*-cresol hydrochloride with dimethyl-*p*-phenylenediamine, crystallises from water, in which it is only sparingly soluble, in small, silky needles melting at 153—154°, and dissolves in acids or alkalis, the alkaline solutions becoming blue on exposure to air. The corresponding *diethyl* compound melts at 74°. p-*Diethylamino*-p-*hydroxydiphenylamine*-m-*carboxylic acid* is precipitated from a solution of its hydrochloride by sodium acetate in the form of a pale yellow, crystalline powder, which melts at 175—177°; the corresponding *dimethyl* acid has the same melting point. All these compounds are converted into blue dyes by fusion with sulphur and sodium sulphide. C. H. D.

Dyes Derived from Protocatechuic Aldehyde. CARL LIEBERMANN (*Ber.*, 1903, 36, 2913—2929. Compare Abstr., 1902, i, 636).—3 : 4-*Dihydroxy*-4′ : 4″-*tetramethyldiaminotriphenylmethane* (*leucoproto-blue*), $C_6H_3(OH)_2\cdot CH(C_6H_4\cdot NMe_2)_2$, obtained by the condensation of protocatechuic aldehyde and dimethylaniline under the influence of zinc chloride, crystallises from benzene in small, colourless needles melting at 164° and almost insoluble in cold alkalis. The *diacetyl* derivative forms colourless needles melting at 141°, and the *dibenzoyl* derivative similar needles melting at 154°.

Methylenedioxy-4′ : 4″-*tetramethyldiaminotriphenylmethane*,

$$CH_2{:}O_2{:}C_6H_3\cdot CH(C_6H_4\cdot NMe_2)_2,$$

obtained in a similar manner from piperonal, crystallises in needles melting at 110—112°.

3 : 4 : 2′ : 2″-*Tetrahydroxy*-4′ : 4″-*tetramethyldiaminotriphenylmethane* (*leucoproto-red*), $C_6H_3(OH)_2\cdot CH[C_6H_3(OH)\cdot NMe_2]_2$, obtained by boiling an aqueous alcoholic solution of protocatechuic aldehyde and *m*-dimethylaminophenol with sulphuric acid, melts at 213°. Its *tetra-acetyl* derivative melts at 165—167°.

Methylenedioxy - 2′ : 2″ - *dihydroxy*-4′ : 4″-*tetramethyldiaminotriphenylmethane*, $CH_2{:}O_2{:}C_6H_3\cdot CH[C_6H_3(OH)\cdot NMe_2]_2$, melts at about 115°.

On oxidation, most of these leuco-compounds yield dyes, which, however, cannot readily be obtained pure on account of the ease with which the free hydroxyl groups also undergo oxidation. When the acetyl derivatives are used, it is found that during oxidation the acetyl compound is hydrolysed. All the colouring matters containing free

hydroxyl groups dye silk directly and cotton when mordanted with the usual oxides.

3 : 4-*Dihydroxytetramethyldiaminotriphenylcarbinol* (*proto-blue*), obtained by the oxidation of the leuco-compound with hydrated manganese dioxide and acetic acid, with sulphuric acid or with lead peroxide forms blue flakes or needles with a metallic green lustre. It dissolves readily in chloroform and also, when freshly prepared, in alcohol. It reacts as a base dissolving in acetic acid to a bluish-red solution, but does not dissolve in cold alkalis. The addition of sodium acetate to a solution of proto-blue in any acid causes the precipitation of the dye. The *hydrochloride* forms a purple, flocculent precipitate and is extremely hygroscopic. The *diacetyl* derivative (*diacetylproto-green*), obtained by the oxidation of the corresponding leuco-compound with lead peroxide, forms a reddish-brown powder. The corresponding *dibenzoyl* derivative forms glistening needles; both compounds dye silk green, but do not combine with the ordinary mordants until after hydrolysis, which occurs readily when alkaline solutions of the compounds are boiled. *Piperonal-green* is also a green dye which does not combine with the usual mordants.

The *compound*, $C_6H_3(OH)_2{\cdot}C[C_6H_3(OH){\cdot}NMe_2]{:}C_6H_3O{\cdot}NMe_2$ (*proto-red*), obtained by the oxidation of the corresponding leuco-compound with manganese dioxide paste and acetic acid, forms a reddish-brown powder soluble in acids, but the salts thus obtained are readily decomposed. It dyes silk red, gives a red dye with alumina mordant and a purple with iron. Its *tetra-acetyl* derivative is green and dyes silk green, but is extremely unstable, and when left in solution overnight is completely transformed into proto-red. The *dibenzoyl* derivative has not been obtained in a pure state.

Dihydroxytetramethylrosaminesulphonic acid,

$$\begin{array}{l} \quad\;\, O\text{——}C_6H_3{=}NMe_2{\cdot}O \\ \quad\;\, | \qquad\quad\;\; | \qquad\qquad\;\; | \\ NMe_2{\cdot}C_6H_3{\cdot}C{\cdot}C_6H_2(OH)_2{\cdot}SO_2 \end{array}$$

is obtained when leucoproto-red is oxidised with concentrated sulphuric acid (compare Biehringer, Abstr., 1897, i, 74). It crystallises in golden-red plates, is practically insoluble in cold water, but dissolves in dilute acetic acid. All solutions exhibit fluorescence, due probably to the fluoran ring. It dyes a bluish-red on silk, cochineal-red on alumina, and an impure red on iron. When boiled with alkali, the sulphuryl group is eliminated and an oily carbinol of dihydroxytetramethylrosamine is formed. J. J. S.

[Tetramethyl-*p*-phenylenediamine.] RICHARD MEYER (*Ber.*, 1903, 36, 2978—2982).—Tetramethyl-*p*-phenylenediamine is conveniently prepared from *p*-phenylenediamine by heating the hydrochloride with methyl alcohol in sealed tubes at 170—180°, finally at 200° for several hours. E. F. A.

New Derivatives of Carbimides. Hydrochlorides of Carbonylhydrazines. SALOMON F. ACREE (*Ber.*, 1903, 36, 3154—3158).—*Carbonyldiphenylhydrazine hydrochloride*, $NPh_2{\cdot}NH{\cdot}COCl$, produced by the interaction of *as*-diphenylhydrazine hydrochloride with sodium hydroxide and phosgene, decomposes on heating at 140° almost

quantitatively into carbonyldiphenylhydrazine and hydrogen chloride, $NPh_2 \cdot NH \cdot COCl \longrightarrow NPh_2 \cdot N:CO + HCl$.

Tetraphenylcarbazide, $NPh_2 \cdot NH \cdot CO \cdot NH \cdot NPh_2$, is formed either by the interaction of *as*-diphenylhydrazine with the theoretical quantity of phosgene in toluene solution, or from carbonyldiphenylhydrazine by boiling it with water or by the addition of diphenylhydrazine. It is colourless when crystallised from alcohol, but becomes blue when exposed to the air; it melts at 239—240°.

Triphenylsemicarbazide, $NPh_2 \cdot NH \cdot CO \cdot NHPh$, formed by the action of aniline on the carbonylhydrazine, melts at 206—207°; it is perhaps identical with the compound melting at 193° obtained by Richter from diphenylhydrazine and phenylcarbimide. E. F. A.

Constitution of Monosemicarbazones and Acetylhydrazones of 1 : 2-Diketones. OTTO DIELS and ARTHUR VOM DORP (*Ber.*, 1903, 36, 3183—3190. Compare Diels, Abstr., 1902, i, 205).—*Acetylpropionylmonosemicarbazone* forms colourless crystals from alcohol melting at 209°. Like the corresponding derivative of diacetyl, it is a weak acid dissolving in alkalis with a yellow coloration and giving a *sodium* derivative, which crystallises in yellow needles, but is immediately dissociated by water.

Acetylpropionylmonoacetylhydrazone is formed by the action of acetic anhydride on the semicarbazone, although it is best prepared by the interaction of acetylpropionyl and acetylhydrazine; it melts at 130° and gives a yellow sodium derivative. When boiled with alkali, it is converted into *methylethylaziethane*, a yellow, crystalline compound melting at 206°.

Phenylmethyldiketonemonosemicarbazone melts at 213° and gives similar alkali derivatives.

Phenylmethyldiketonemonoacetylhydrazone, melting at 154°, shows the same properties as its analogues.

Diacetylmonoacetylhydrazone methyl ether, $C_7H_{12}O_2N_2$, is prepared by the interaction of methyl iodide and the potassium salt of the hydrazone in sealed tubes at 100°; it crystallises from light petroleum in white prisms melting at 43°, is easily soluble in most organic solvents, but at once decomposed by water, acids, or alkalis. When heated with water, it is resolved into diacetyl and a colourless, crystalline compound melting at 98°.

The *methyl ether* of acetylpropionylmonoacetylhydrazone behaves in a similar manner; it melts at 47°.

Camphorquinone monosemicarbazone (Lapworth and Chapman, Proc., 1902, 18, 28) dissolves in dilute alkalis with a yellow coloration and is reprecipitated unchanged by acetic acid. Benzilmonosemicarbazone dissolves, forming colourless solutions, but acids precipitate diphenyloxytriazine from the solution. The formation of the yellow alkali derivatives here described is attributed to the presence of the oxyvinyl group. E. F. A.

Diketones and Tetraketones from *p*-Aminoacetophenone. CARL BÜLOW and ERNST NOTTBOHM (*Ber.*, 1903, 36, 2695—2700).—Taking into account the results obtained by Bülow and Wagner (this

vol., i, 647), the authors conclude that the *iso*oxazole supposed in a previous paper (this vol., i, 274) to have the constitution

$$\begin{matrix} CO_2Et\cdot C\colon CMe \\ CO_2Et\cdot C\colon CMe \end{matrix} > N\cdot C_6H_4\cdot C \lessdot \begin{matrix} N—O \\ CH\colon C\cdot CO_2Et \end{matrix},$$

has really the structure

$$\begin{matrix} CO_2Et\cdot C\colon CMe \\ CO_2Et\cdot C\colon CMe \end{matrix} > N\cdot C_6H_4\cdot C \lessdot \begin{matrix} O—N \\ CH\cdot C\cdot CO_2Et \end{matrix}.$$

The following substances are analogous to compounds which have already been described. *Ethyl* p-*acetylaminobenzoylpyruvate*,

$$NHAc\cdot C_6H_4\cdot C(OH)\colon CH\cdot CO\cdot CO_2Et,$$

prepared by condensing *p*-acetylaminoacetophenone with ethyl oxalate by means of sodium, crystallises from acetone in well-formed, yellow needles and melts indefinitely between 80° and 124°; the *copper* derivative crystallises from alcohol in green needles. With hydroxylamine, the ester gives rise to the *monoxime*, $C_{14}H_{16}O_5N_2$, crystallising in colourless needles and melting at 177—178°, and *ethyl* 5-p-*acetylaminophenyl*isooxazole-3-*carboxylate*, $NHAc\cdot C_6H_4\cdot C \lessdot \begin{matrix} O—N \\ CH\cdot C\cdot CO_2Et \end{matrix}$, which separates in thick crystals. The ester also combines with benzenediazonium chloride forming *ethyl benzeneazo*-p-*acetylaminobenzoylpyruvate*, $NHAc\cdot C_6H_4\cdot C(OH)\colon C(N_2Ph)\cdot CO\cdot CO_2Et$, which crystallises from dilute alcohol in brownish-red needles and melts at 123—124°. p-*Acetylaminobenzoylpyruvic acid*, prepared by hydrolysing the ester, crystallises from glacial acetic acid or water in green needles and melts at 221·5°.

Ethyl oxalylbis-p-*aminobenzoylpyruvate*,

$$C_2O_2[NH\cdot C_6H_4\cdot C(OH)\colon CH\cdot CO\cdot CO_2Et]_2,$$

prepared by condensing *p*-aminoacetophenone with ethyl oxalate (4 mols.) by means of sodium, crystallises from glacial acetic acid in microscopic needles, begins to melt at 151°, and decomposes at 180—191°; when heated with aqueous sodium hydroxide, it is resolved into *p*-aminoacetophenone, alcohol, and oxalic acid. W. A. D.

Action of Formaldehyde on Ethyl Nitromalonate and on Nitromalonamide. C. ULPIANI and E. PANNAIN (*Gazzetta*, 1903, **33**, i, 379—393).—The action of formaldehyde on the ammonium derivative of ethyl nitromalonate yields a *compound*,

$$CH_2\colon C \lessdot \begin{matrix} C(CO_2Et)\colon NO\cdot O \\ C(CO_2Et)\colon NO\cdot O \end{matrix} > CH_2,$$

which separates from alcohol in rather oily, yellow crystals and from acetic acid in small, white crystals melting at 46°; it is soluble in ether or concentrated hydrochloric acid, from which it crystallises unchanged; by treatment with ammonia and formaldehyde, it yields 5-*methylenehexahydropyrimidide*-4 : 6-*dicarboxylamide*,

$$CH_2\colon C \lessdot \begin{matrix} CH(CO\cdot NH_2)\cdot NH \\ CH(CO\cdot NH_2)\cdot NH \end{matrix} > CH_2,$$

which is soluble in water, alcohol, or ethyl acetate, and crystallises from the last of these in white needles, subliming unaltered at about 170°; it has the normal molecular weight in boiling water, with which it gives a neutral solution. It forms the following double compounds : with

mercuric chloride, $C_7H_{12}O_2N_4,HgCl_2$, crystallising from water or alcohol in white needles, melting and decomposing at 187°; with *silver nitrate*, $C_7H_{12}O_2N_4,AgNO_3$, a white, crystalline precipitate becoming faintly greyish-yellow in the light and melting at about 206°. Its *hydrochloride* forms white, monoclinic crystals melting and decomposing at about 196°, whilst its *hydriodide* crystallises from alcohol in pale yellow needles melting at about 202°. The action of nitrous acid on the amide not only converts the NH group into N(NO), but also removes a labile methylene group, the result being a *nitroso*-compound, $C_6H_{10}O_4N_6$, soluble in water, chloroform, ethyl acetate, or alcohol, from the last of which it crystallises in rectangular plates or hexagonal prisms melting at 192—193°. In acetic acid or aqueous solution, the amine absorbs bromine, giving a *compound*, $C_9H_{12}O_2N_4Br_2$, which separates in yellow, prismatic needles; when heated with water, alcohol, or acetic acid, this bromo-compound loses bromine and gradually dissolves forming the *hydrobromide* of the amide, which separates in triangular or hexagonal prisms melting at about 196°.

The amide is also obtained, in almost theoretical yield, by the action of ammonia and formaldehyde on nitromalonamide. T. H. P.

Action of Acetic Anhydride and Sulphuric Acid on Nitroaminobenzyl-*p*-nitraniline. OTTO STILLICH (*Ber.*, 1903, 36, 3115—3121).—In the preparation of nitroaminobenzyl-*p*-nitraniline (Abstr., 1902, i, 319), it is best to use sodium carbonate to liberate the base. When the base is boiled for a short time with excess of acetic anhydride and concentrated sulphuric acid and then cooled and mixed with alcohol, it yields 3-p-*nitrophenyl*-2-*methyl*-6-*nitro*-3 : 4-*dihydroquinazoline sulphoacetate*, $C_{15}H_{12}O_4N_4,C_2H_4O_5S$, which crystallises from acetic anhydride in yellow prisms decomposing at 268°. It is extremely hygroscopic, but is insoluble in water.

An isomeric salt decomposing at 214° is obtained when only a few drops of sulphuric acid are employed. This salt crystallises from acetic anhydride in characteristic pointed plates. Both salts, on treatment with dilute alkalis, yield the same base, 6-*nitro*-3-p-*nitrophenyl*-2-*methyl*-3 : 4-*dihydroquinazoline*, $\begin{array}{l}NO_2\cdot C\!:\!CH—C\cdot CH_2\cdot N\cdot C_6H_4\cdot NO_2 \\ \quad\ CH\!:\!CH\cdot C\cdot N═CMe\end{array}$. It crystallises from acetone in reddish-yellow plates, sinters at 185°, melts at 188—191°, and dissolves in chloroform, hot alcohol, ethyl acetate, or benzene, but is only sparingly soluble in ether and is insoluble in water. The *hydrochloride*, $C_{15}H_{12}O_4N_4,HCl$, is readily soluble and decomposes about 300°. The *sulphate*, $C_{15}H_{12}O_4N_4,H_2SO_4$, crystallises from water and decomposes at 265—267°. The *nitrate* decomposes at 178°.

When the salt decomposing at 268° is boiled with water and acetic acid and then crystallised from acetone, 6-*nitro*-2-*hydroxy*-3-p-*nitrophenyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline* is obtained,

$$\begin{array}{l}NO_2\cdot C═CH\cdot C\cdot CH_2\cdot N\cdot C_6H_4\cdot NO_2 \\ \quad\ CH\!:\!CH\cdot C\cdot NH\cdot CMe\cdot OH\end{array}.$$

It melts at 243—246° and is the same compound as was previously described as acetylnitroaminobenzyl-*p*-nitroaniline. Hydrochloric acid

transforms it into 2-chloro-6-nitro-3-*p*-nitrophenyl-2-methyl-1 : 2 : 3 : 4-tetrahydroquinazoline. J. J. S.

Action of Bromine on Aromatic Thiocarbamides. A. Hugershoff (*Ber.*, 1903, 36, 3121—3134. Compare Abstr., 1901, i, 757 and 758).—The product obtained by the action of bromine on phenylthiocarbamide in chloroform solution, when treated with sulphurous acid, yields Hofmann's aminothiocarbimide (Abstr., 1879, 806, and 1880, 387), which, according to Hantzsch, is 1-aminobenzothiazole. When diphenylthiocarbamide is employed, anilinobenzothiazole is formed (compare Hofmann, and also Jacobson and Frankenbacher, Abstr., 1891, 1048). The compound obtained from acetyldiphenylthiocarbamide is the acetyl derivative of 1-anilinobenzothiazole.

Mono-, di-, or tri-substituted derivatives of thiocarbamide react with a chloroform solution of bromine in a similar manner, yielding thiazolone derivatives, thus indicating the tendency of sulphur to combine with carbon in the ortho-position with respect to an amino-group.

The bromine *compound*, $C_{13}H_{10}N_2SBr_4$, obtained by the action of a chloroform solution of bromine on diphenylthiocarbamide, forms brick-red needles, melts at 136°, and on exposure to the air loses part of the bromine. When crystallised from alcohol or left in contact with water, or even better with dilute sodium hydroxide, it yields a *dibromo*-derivative of 1-anilinobenzothiazole, which forms a voluminous white powder melting at 195°. Sulphurous acid or sodium hydrogen sulphite transform the tetrabromo-compound into a salt of 1-anilinobenzothiazole.

1-o-*Toluidino-3-methylthiazole*, $C_6H_3Me{<}{\substack{N\\S}}{>}C{\cdot}NH{\cdot}C_6H_4Me$, obtained in a similar manner, crystallises from alcohol in short, thick prisms, melts at 136—137°, yields a *hydrochloride* melting at 245—248°, and an *acetyl* derivative melting at 77°.

Acetyldi-*o*-tolylthiocarbamide reacts with a chloroform solution of bromine, yielding brick-red crystals, which, on exposure to the air, lose part of their bromine, and thus become transformed into a yellow, crystalline powder, $C_{17}H_{16}ON_2SBr_4$; on treatment with sulphurous acid, the bromine compound is transformed into 1-acetyl-*o*-toluidino-3-methylthiazole, melting at 77°.

p-*Toluidino-3-methylthiazole* crystallises from alcohol in long, fibrous needles melting at 162° and yields an *acetyl* derivative melting at 158°.

An alcoholic solution of diphenylthiocarbamide yields with bromine 3 : 5-diphenylimino-4 : 2-diphenyl-tetrahydro-1 : 2 : 4-thiodiazole, which is identical with Hector's miazthiazole derivative (Abstr., 1890, 526). It melts at 135—136°.

3 : 5-*Di*-p-*toluidino*-4 : 2-*di*-p-*tolyl-tetrahydro*-1 : 2 : 4-*thiodiazole*, $C_{30}H_{28}N_4S$, melts at 139°, is only sparingly soluble in alcohol, and practically insoluble in ether or light petroleum.

The chief product obtained by the action of bromine on an alcoholic solution of di-*o*-tolylthiocarbamide is 1-*o*-toluidino-3-methylthiazole hydrobromide. J. J. S.

Identity of the Thiocarbazines and Thiazoles. A. HUGERSHOFF (*Ber.*, 1903, 36, 3134—3138).—1-Aminobenzothiazole (see preceding abstract), phenylthiocarbizine, prepared by Fischer and Besthorn (Abstr., 1882, 1091) by heating phenylthiosemicarbazide with 20 per cent. hydrochloric acid, and the so-called aminothiocarbimide, obtained by Hofmann from phenylthiocarbimide by the action of phosphorus pentachloride, and subsequently of alcoholic ammonia, are proved to be identical as they all melt at 129°, form methyl derivatives melting at 123°, bromine derivatives melting at 210°, and acetyl and benzoyl compounds melting at 186—187° and 186° respectively.

The formation of this compound, $C_6H_4<\begin{matrix}NH\\S\end{matrix}>C:NH$, from phenylthiosemicarbazide can be explained on the assumption that a nitrogen from the hydrazine complex is separated as ammonia; it is thus analogous to Fischer's indole synthesis from hydrazine derivatives. To account for the formation of the phenylmethylthiocarbizines studied by Harries and Lowenstein (Abstr., 1895, i, 304), rearrangement and subsequent elimination of methylaniline must be assumed.

E. F. A.

Aryl Derivatives of Alkyl*iso*rosindulines. LEOPOLD CASSELLA & Co. (D.R.-P. 142947).—Reducing agents convert alkyl*iso*rosindulines into leuco-bases. Sodium sulphide, however, forms sulphur compounds of undetermined constitution. Thus the diethylated-neutral-blue, $C_{10}H_6<\begin{matrix}N\\NClPh\end{matrix}>C_6H_3\cdot NEt_2$, reacts with sodium sulphide in alcoholic solution, forming a crystalline derivative containing one atom of sulphur in the molecule. This substance is insoluble in water and the organic solvents, but dissolves to a slight extent in dilute sulphuric acid yielding an intensely blue solution. When heated with aromatic amines, the new thio-compound evolves hydrogen sulphide and yields a safranine derivative which dissolves in concentrated sulphuric acid to an emerald-green solution. This compound and its analogues give blue or violet alcoholic solutions with a brown fluorescence and yield soluble sulpho-derivatives having important tinctorial properties.

C. H. D.

Preparation of Dimethyl- and Diethyl-aminophenyldimethylpyrazolone. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 144393).—The formation of quaternary derivatives in the alkylation of amino-1-phenyl-2:3-dimethyl-5-pyrazolone is avoided by the use of chloro- or bromo-acetic or propionic acid as alkylating agents, with the addition of sodium carbonate or acetate. The *diacetic acid*, $C_{11}H_{11}ON_2\cdot N(CH_2\cdot CO_2H)_2$, and the corresponding *dipropionic acid* are fairly strong acids, and are not set free from their salts by acetic acid. They dissolve in mineral acids. Their *sodium* salts are precipitated by ether from their alcoholic solutions as highly deliquescent crystals. When heated with dilute mineral acids at 130—140° under pressure, they decompose into carbon dioxide and the dialkyl derivatives. The product of the alkylation may also

be heated with acids directly, without isolation of the intermediate product. C. H. D.

Constitution of Phenylurazoles. II. Reactions with Diazomethane. Salomon F. Acree (*Ber.*, 1903, 36, 3139—3154. Compare Abstr., 1902, i, 242).—Phenylurazole is shown to be *3-hydroxy-5-keto-1-phenyl-4 : 5-dihydrotriazole*, $\begin{matrix}\mathrm{NPh-N}\\ \mathrm{CO\cdot NH}\end{matrix}\!\!>\!\mathrm{C\cdot OH}$. By the action of silver nitrate on the monoalkali-derivative, a *disilver* derivative, $C_2N_3Ph(OAg)_2$, is obtained, which, on treatment with ethyl iodide, yields Wheeler's 3-ethoxy-5-keto-1-phenyl-4 : 5-dihydrotriazole melting at 152° (Abstr., 1900, i, 563). This, when heated with methyl iodide, forms *3-ethoxy-5-keto-1-phenyl-4-methyl-4 : 5-dihydrotriazole*, which melts at 95° and, on hydrolysis, yields the 3-hydroxy-compound melting at 223° (compare *loc. cit.*); thus the ethoxy-group is in position 3 and not 5.

3 : 5-Diethoxy-1-phenyl-4 : 5-dihydrotriazole, $\begin{matrix}\mathrm{NPh\cdot N}\\ \mathrm{OEt\cdot C{=\!=}N}\end{matrix}\!\!>\!\mathrm{C\cdot OEt}$, crystallises from alcohol in needles melting at 53° and shows marked electrical properties.

3-Methoxy-5-keto-1-phenyl-4-methyl-4 : 5-dihydrotriazole, best produced by the action of diazomethane in ethereal solution on phenylurazole, crystallises from alcohol in needles melting at 95° and is hydrolysed by acids to the 3-hydroxy-derivative melting at 223°. These experiments show that in phenylurazole one hydrogen atom is in position 4 and that the hydroxyl group is in position 3.

3-Methoxy-5-keto-1-phenyl-4 : 5-dihydrotriazole, formed when an ethereal diazomethane solution is allowed to drop on to solid phenylurazole, crystallises in plates melting at 197°.

2-Acetyl-1-phenyl-4-methylurazole, $\begin{matrix}\mathrm{NPh\cdot NAc}\\ \mathrm{CO-NMe}\end{matrix}\!\!>\!\mathrm{CO}$, obtained by the action of diazomethane on acetyl phenylurazole, crystallises from alcohol in needles which melt at 94°, or, after prolonged heating to 140°, at 114—115°.

3-Thiol-5-keto-1-phenyl-4 : 5-triazole, obtained by the hydrolysis of α-ethyl phenylthiosemicarbazidecarboxylate with alkali, is a yellow powder melting at 195°. It is a monobasic acid, forms a coloured salt with ferric chloride, and a red solution with concentrated sulphuric acid. Phenylthiourazole can be quantitatively titrated either with alkali or iodine.

It can be directly esterified either by methyl alcoholic hydrochloric acid or with methyl iodide or diazomethane. *3-Methylthiol-5-keto-1-phenyl-4 : 5-dihydrotriazole* melts at 178°, whereas the *3-ethylthiol* derivative melts at 138°.

3-Methylthiol-5-keto-1-phenyl-4-methyl-4 : 5-dihydrotriazole can be obtained from the preceding compound in various ways; it melts at 95°. E. F. A.

New Cyanuric Acid Compounds. Otto Diels and Max Liebermann (*Ber.*, 1903, 36, 3191—3197).—*Tri-p-ethoxycyaphenine* [*2 : 4 : 6-tri-p-ethoxyphenyl-1 : 3 : 5-triazine*], $C_3N_3(C_6H_4\cdot OEt)_3$, prepared

by the interaction of cyanuric chloride and *p*-bromophenetole, crystallises in faintly yellow-coloured plates from acetic ether melting at 171° (corr.). When hydrolysed by heating with aluminium chloride, it forms *tri-p-hydroxycyaphenine*, $C_3N_3(C_6H_4{\cdot}OH)_3$, yellow needles melting at 357° (corr.), but the amount of this is very small. *Di-p-ethoxyphenylcyanuric chloride*, $C_3N_3Cl(C_6H_4{\cdot}OEt)_2$, formed at the same time as the triethoxy-derivative, crystallises from benzene in colourless clusters of needles melting at 149° (corr.).

Diethoxycyanuric chloride, $C_3N_3(OEt_2)Cl$, formed by the reduction of pure cyanuric chloride dissolved in alcohol with zinc dust, is obtained as an oil boiling at 144—145° under 12—14 mm. pressure. It crystallises from benzene in stellar aggregates of needles melting at 43—44°. The *dimethoxy*-derivative sinters at 78° and melts at 81°. *Dimethylmonothiolcyanurate*, $SH{\cdot}C_3N_3(OMe)_2$, crystallises in prisms from alcohol, which, on heating, sinter at 130°, melt at 134° (corr.), and then again at 194° (corr.). *Monothiolcyanuric acid*, $SH{\cdot}C_3N_3(OH)_2$, prepared by hydrolysing the ester with dilute hydrochloric acid, melts at 316° (corr.) and forms a characteristic mercury salt. E. F. A.

Preparation of a Sulphur Dye. KALLE & Co. (D.R.-P. 144157.) —4-Nitro-2-amino-4′-hydroxydiphenylamine condenses with nitrosodimethylaniline in alkaline solution to form a dye of the azine group, dissolving in alkalis, but forming no diazonium compound, and probably having the constitution $OH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_2(NO_2){<}^{N}_{N}{>}C_6H_3{\cdot}NMe_2$. This is a violet-black powder, almost insoluble in water, and dissolving in dilute hydrochloric acid to a reddish-violet solution. When fused with sulphur and sodium sulphide, a dye is formed which dissolves in water to a dark green solution. The violet shade of the dye is deepened by the action of oxidising agents. C. H. D.

Preparation of Xanthine. C. F. BOEHRINGER and SÖHNE (D.R.-P. 143725).—Nitrous acid oxidises the alkylthioxanthines to alkylxanthines (see Abstr., 1901, i, 770). It is now found that thioxanthine may be oxidised to xanthine by means of sodium nitrite in fuming hydrochloric acid solution, or by hydrogen peroxide in alkaline solution, or by manganese dioxide in neutral solution. The sulphur is eliminated as sulphur dioxide or as sulphuric acid, according to the oxidising agent employed. C. H. D.

Diazotisation of Difficultly Diazotisable Amines. PAUL SEIDLER (D.R.-P. 143450).—The diazotisation of difficultly soluble amino-compounds, especially when the diazonium salt formed is also insoluble, cannot be effected by the employment of an excess of nitrous acid, because, on account of the sparing solubility of this acid in water, it escapes without entering into reaction. This is avoided by working under increased pressure. The compound to be diazotised is introduced into a closed vessel, together with the corresponding

quantity of mineral acid, and the pressure is then raised by pumping in air or other indifferent gas, after which the nitrite solution is added.

C. H. D.

Liquid Crystals. TH. ROTARSKI (*Ber.*, 1903, 36, 3158—3163).—It is shown that *p*-azohydroxyanisole, prepared by the reduction of *p*-nitroanisole dissolved in methyl alcohol with sodium methoxide, is in reality a mixture of *p*-azoanisole, melting at 160—162°, and *p*-azoxyanisole, melting at 144—146°. Both these substances, when pure, melt to clear liquids; their mixture, however, is cloudy when melted and when viewed between crossed Nicols brightens the field of vision. This phenomenon, which has been described by Lehmann under the term "liquid crystals," is therefore due to the optical properties of the mixture (perhaps an emulsion) only. As another instance, *p*-azophenetole is adduced: when pure, it melts to a clear liquid; when less carefully purified, the melted liquid is cloudy.

E. F. A.

Decomposition of Diazo-ethers. ARTHUR HANTZSCH (*Ber.*, 1903, 36, 3097—3102. Compare Euler, this vol., i, 212, 722).—The aqueous extracts obtained by shaking an ethereal solution of *p*-bromobenzene-*anti*diazomethyl ether with small amounts of water are capable of yielding dyes with α- or β-naphthol. When the operation has been repeated several times, the extract no longer "couples" with the naphthols, but if the extraction is repeated with dilute sodium hydroxide solution, the first extracts are again capable of combining with naphthols, but not the later, and the ethereal solution left is relatively stable towards water and dilute alkalis. The products removed by shaking with water are regarded as decomposition products and not as ordinary products of hydrolysis. The primary decomposition products are a primary arylamine and methyl nitrite formed according to the equation $ArN\vdots N\cdot OMe + H_2O = ArNH_2 + NO\cdot OMe$. On treatment with water, these can react to form a diazonium nitrite, and on treatment with alkali it is well known that the compounds give a normal diazoxide which can "couple" up with naphthols. The two decomposition products mentioned above have been actually isolated.

The formation of these primary decomposition products favours the *anti*diazo-constitution of the ethers and renders explicable Bamberger's results, as the extracts examined by Bamberger contained these decomposition products or products derived from them and not the diazo-ethers or their true hydrolytic products. At the ordinary temperature, the true hydrolysis takes place, but to a much more limited extent than the above-mentioned decomposition. At 0°, the decomposition is retarded and the hydrolysis becomes more readily observable, and the formation of an *anti*diazoxide can be shown. It has been found that β-naphthol can be used for the separation of *syn*- and *anti*-diazoxides.

J. J. S.

The Process of Dyeing. II. ARTHUR BINZ and GEORG SCHROETER (*Ber.*, 1903, 36, 3008—3014. Compare this vol., i, 109).—Pure wool and silk with a neutral reaction are not dyed by azobenzenesulphonic acid in neutral or alkaline solution, as Georgievics has stated (*Zeit. Farb. Text. Chem.*, 1903, 2, 215), although the fibre is able to absorb the free acid even from a strongly acid solution. Azobenzene-*p*-carboxylic acid, however, which dyes wool a yellow colour in neutral solution, is not absorbed by the fibre in acid or in alkaline solution. It is suggested that the dyeing is due to salt-formation between the dye and the fibre, and that the sulphonic acid is able to compete with a mineral acid for the basic radicle of the fibre, whilst the feeble carboxylic acid is completely displaced by mineral acids.

p-Hydroxy- and *o-p*-dihydroxy-azobenzenes, on the other hand, are absorbed in neutral acid and alkaline solution, the absorption being only slightly reduced by excess of alkali when the latter is beginning to act on the wool. These are regarded as combining in the quinonoid form with the fibre, possibly forming an additive compound of the quinhydrone type.

Di-*m*-amino- and tetramethyldi-*m*-amino-azobenzenes and *p*-azobenzenetrimethylammonium hydroxide are not capable of existing in a quinonoid form, and can only combine with the fibre by salt-formation. The two former are not absorbed in presence of 6—10HCl, but their salts are partially hydrolysed in less strongly acid solution, and the free base is absorbed by the fibre; the latter, a very much stronger base, is not absorbed from neutral, and still less from acid, solutions.

p-Amino- and *p*-dimethylamino-azobenzenes, chrysoidine and Bismarck brown, which are capable of existing in quinonoid forms, are absorbed by the fibre even in presence of 120HCl; the quantity of the two former absorbed is slightly reduced by excess of acid, but the two latter give an even deeper colour in acid than in neutral solution.

T. L. M.

Alkylated Azo-compounds and the Theory of Dyeing. RICHARD MEYER and JOHANN MAIER (*Ber.*, 1903, 36, 2970—2978. Compare Abstr., 1895, i, 135).—On ethylation, *diphenylbisazophenol* yields a *monoethyl ether*, $C_{24}H_{17}ON_4\cdot OEt$, which crystallises in olive-coloured plates, melts at 272°, and dissolves in alcoholic sodium hydroxide with a red colour, and a *diethyl ether*, $C_{24}H_{16}N_4(OEt)_2$, which crystallises in reddish-yellow plates, melts at 252—253°, and is quite insoluble in alkalis. Similarly, the *monobenzyl ether* forms olive-coloured crystals, whereas the *dibenzyl ether* is bright red.

Crysophenin, obtained by the ethylation of "brilliant-yellow," is now shown to be the *diethyl ether*, $C_{30}H_{28}O_8N_4S_2$, and not the monoether as previously supposed. It forms a sparingly soluble sodium salt. On alkylation, "brilliant-yellow" yields a mixture of both mono- and di-ethers, which can be separated by reason of their different solubility in alcoholic sodium hydroxide; similarly, it forms a mixture of *mono-* and *di-benzyl ethers* separable in like manner.

Further, commercial "diamine-gold" is the diethyl ether of

naphthalenedisulphobisazophenol. In every case, therefore, mono- and di-alkyl ethers are produced simultaneously on alkylating symmetrical hydroxyazo-compounds. E. F. A.

Constitution of Mixed Azo-compounds. I. Knorr's Phenylmethylpyrazoloneazobenzene. ALEXANDER EIBNER (*Ber.*, 1903, 36, 2687—2692).—After discussing the structure of Knorr's phenylmethylpyrazoloneazobenzene (Abstr., 1888, 724), the following facts are brought forward as supporting the azo-formula,

$$NPh{<}\begin{matrix}N{=}CMe\\ CO\cdot CH\cdot N{:}NPh\end{matrix}.$$

When benzenediazonium chloride (1 mol.) is added to a solution of phenylmethylpyrazolone (1 mol.) in aqueous sodium hydroxide (2 mols.), the golden-yellow, crystalline *sodium* salt, $NPh{<}\begin{matrix}N{=}CMe\\ C(ONa){:}C\cdot N{:}NPh\end{matrix}$, is formed; its solution is readily decomposed by carbon dioxide, giving Knorr's compound, thus:

$$\text{I. } NPh{<}\begin{matrix}N{=}CMe\\ C(ONa){:}C\cdot N{:}NPh\end{matrix} \longrightarrow \text{II. } NPh{<}\begin{matrix}N{=}CMe\\ C(OH){:}C\cdot N{:}NPh\end{matrix}$$
$$\longrightarrow \text{III. } NPh{<}\begin{matrix}N{=}CMe\\ CO\cdot CH\cdot N{:}NPh\end{matrix}.$$

The intermediate formula, II, is held to be unlikely for the azo-compound, seeing that this substance can be heated for 2 hours with acetic anhydride containing a drop of sulphuric acid without acetylation occurring.

When to phenylmethylpyrazoloneazobenzene dissolved in chloroform bromine is added, orange-red needles of a *perbromide* separate, whilst hydrogen bromide is not formed until the end of the action; in this respect, the action of bromine is similar to that which occurs with azobenzene, and differs from its action on benzaldehydephenylhydrazone.
W. A. D.

Precipitation Limits with Ammonium Sulphate of some Vegetable Proteids. THOMAS B. OSBORNE and ISAAC F. HARRIS (*J. Amer. Chem. Soc.*, 1903, 25, 837—842).—It has been shown by Hofmeister that under suitable conditions the individual proteids are precipitated by ammonium sulphate within narrow limits which, to a certain extent, are characteristic for each proteid. The authors have determined these limits for the following proteids: the globulin of the English walnut, globulin of the black walnut, edestin, edestin monochloride, globulin of flax seed, globulin of the castor bean, globulin of squash seed, amandin, corylin, excelsin, conglutin *a*, conglutin *b*, globulin of cotton seed, legumin, and phaseolin.

The crystalline globulins of the squash seed, flax seed, and castor bean resemble that of hemp seed so closely that until recently they have been regarded as identical, and it is found that this similarity extends to their precipitation limits by ammonium sulphate. The globulin of the cotton seed has different precipitation limits from

edestin of hemp seed. The globulin of the filbert (*Corylus tubulosa*) and that of the English walnut (*Juglans regia*) were described by Osborne and Campbell (Abstr., 1896, i, 716) under the name of "corylin." Recently, however, it has been shown (*J. Amer. Chem. Soc.*, 1903, 25, 323) that these globulins must be regarded as distinct substances, and this conclusion is now confirmed by the determination of their precipitation limits. The name "corylin" should, therefore, be applied only to the globulin of the filbert. The globulin of the American black walnut showed the same behaviour with ammonium sulphate as that of the English walnut. Excelsin from the Brazil nut and amandin from the almond, although different substances, have nearly the same precipitation limits. Preparations of legumin from vetch seeds, horse bean, and lentil showed the same precipitation limits. The seeds of the yellow lupin contain two proteids, conglutin α and conglutin b, which can be separated by fractional precipitation. The globulin from the blue lupin showed nearly the same behaviour as the less soluble globulin (conglutin α) of the yellow lupin. E. G.

Specific Rotation of some Vegetable Proteids. THOMAS B. OSBORNE and ISAAC F. HARRIS (*J. Amer. Chem. Soc.*, 1903, 25, 842—848). —The specific rotatory power, $[\alpha]_D$ at 20°, of a number of vegetable proteids has been determined with the following results: edestin from hemp seed, $-41·3°$; globulin of flax seed, $-43·53°$; globulin of squash seed, $-38·73°$; excelsin from the Brazil nut, $-42·94°$; amandin from almonds, $-56·44°$; corylin from the filbert, $-43·09°$; globulin of the English walnut, $-45·21°$; globulin of the black walnut, $-44·43°$; phaseolin from the kidney bean, $-41·46°$; legumin from the horse bean, $-44·09°$; zein from maize, $-28·00°$; gliadin from wheat, $-92·28°$.

The differences in the rotatory power of edestin, flax seed globulin, and squash seed globulin confirm the view already expressed (*J. Amer. Chem. Soc.*, 1903, 25, 323) that they are distinct substances. The specific rotatory powers of the globulin of the English walnut and that of the filbert show another difference between these two very similar proteids. The globulins of the American black walnut and the English walnut show practically the same rotatory power. E. G.

Globulin of the English Walnut, the American Black Walnut and the Butternut. THOMAS B. OSBORNE and ISAAC F. HARRIS (*J. Amer. Chem. Soc.*, 1903, 25, 848—853).—A comparative examination has been made of the globulins from the English walnut (*Juglans regia*), the black walnut (*J. nigra*), the butternut (*J. cinerea*), and the filbert (*Corylus tubulosa*). The results show that corylin from the filbert yields a larger quantity of nitrogen as ammonia than the globulin from the other three seeds. The precipitation limits of corylin with ammonium sulphate and its specific rotatory power also indicate that this proteid is different from the globulin of the other seeds. It is therefore suggested that the name "corylin" should be retained for the globulin of *Corylus*, and that the principal proteid of the nuts of the three species of *Juglans* should be termed "*juglansin*." E. G.